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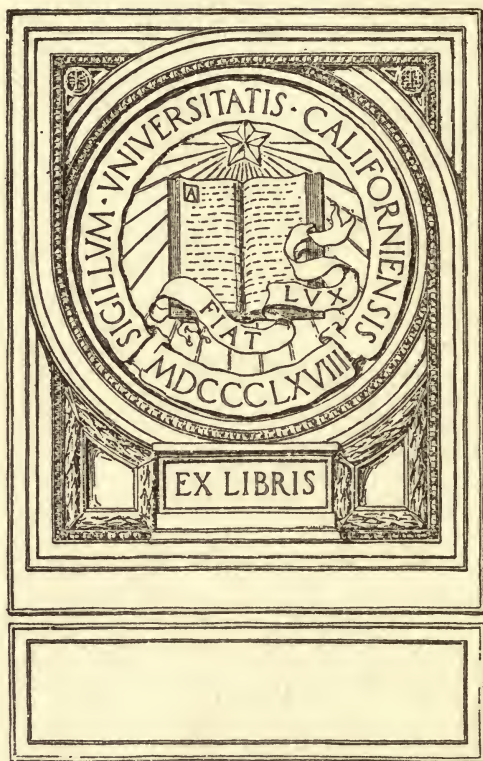


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THE ANALYTICAL CHEMISTRY  
OF THE  
RARER ELEMENTS

L. J. CURTMAN

YC 21848







AN INTRODUCTION  
TO THE  
ANALYTICAL CHEMISTRY  
OF THE  
RARER ELEMENTS

BY

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## PREFACE

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THE experiments described in this book are designed to lay a sound foundation for the analytical study of the rarer elements. The great economic importance attained by these metals in the last decade indicates the imperative need of introducing into our colleges and universities a course of instruction such as is given in this book. Lectures and text-book study unsupported by adequate laboratory practice are ineffective in this essentially experimental field. The author wishing to give his students a brief laboratory course in the rarer elements in which the analytical side would be emphasized, looked about in vain for a suitable text. He therefore prepared this series of experiments to meet his requirements. *Every experiment described in this manual was personally performed and repeated by the author.* As is well known, the results obtained in preliminary experiments in qualitative analysis depend not only upon the concentrations of the test-solutions used, but also upon the strengths of the reagents employed. To this end, test-solutions of known concentrations are invariably employed. The preparation of these solutions is facilitated by the use of the author's special table giving the quantities of the salts or compounds to be used in each set of experiments. To insure further definiteness in the results, directions are given for preparing the reagents to be used in making the tests.

A laboratory course in the rarer elements is often objected to on the ground that the materials required are expensive. To meet this difficulty, it was necessary first, to provide that in each test a *very small* though *definite* quantity of metal be used; second, to carry out numerous experiments to determine the conditions under which conclusively visible results could be obtained when using small amounts of metal. Both of these tasks have been successfully accomplished. From the total quantity of material used in any series of experiments, it will be apparent that even with

large classes, the cost of the material will not be considerable. To further reduce the cost, provision should be made to recover the more expensive metals from the students' waste solutions.

This book may be used to complete a one-year course in Qualitative Analysis. Or it may serve as an introductory text in a special course on the rarer elements in which lectures are given, analyses made, and in which provision is made for consulting the fairly rich literature of this subject.

The author will be grateful for constructive criticism or suggested improvements.

L. J. C.

NEW YORK CITY,  
Oct., 1921.



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## REFERENCE BOOKS ON THE RARER ELEMENTS

- CROOKES. Select Methods in Chemical Analysis.
- CLASSEN. Ausgewählte Methoden der analytischen Chemie.  
Erster Band.
- FRESENIUS. Qualitative Chemical Analysis. Translated by  
Mitchell, 1921.
- SCHOELLER AND POWELL. The Analysis of Minerals and Ores of  
the Rarer Elements.
- BROWNING. Introduction to the Rarer Elements.
- A. A. NOYES. Technology Quarterly, **16**, 93-131, **17**, 214-257.
- A. A. NOYES AND BRAY. Journal Amer. Chem. Society, **29** (1907),  
137-205.
- A. A. NOYES, BRAY AND SPEAR. Journal Amer. Chem. Society,  
**30** (1908), 481-563.
- NEWTON-FRIEND. Text-book of Inorganic Chemistry. 10 vols.
- ROSCOE AND SCHORLEMMER. Treatise on Chemistry. (Vols. 1  
and 2.)
- ABEGG. Handbuch der anorganischen Chemie.
- SPENCER. The Metals of the Rare Earths.
- R. J. MEYER AND O. HAUSER. Die Analyse der seltenen Erden  
und der Erdsäuren.
- BÖHM. Die Darstellung der seltenen Erden. (2 vols.)
- TRUCHOT. Les Terres Rares.
- HERZFELD AND KORN. Chemie der seltenen Erden.

# INTERNATIONAL ATOMIC WEIGHTS, Corrected to 1920

Name	Sym- bol.	Atomic Weight.	Name	Sym- bol.	Atomic Weight.
Aluminum.....	Al	27.1	Molybdenum.....	Mo	96.0
Antimony (Stibium)	Sb	120.2	Neodymium.....	Nd	144.3
Argon.....	A	39.9	Neon.....	Ne	20.2
Arsenic.....	As	74.96	Nickel.....	Ni	58.68
Barium.....	Ba	137.37	Nitron.....	Nt	222.4
Bismuth.....	Bi	208.0	Nitrogen.....	N	14.01
Boron.....	B	10.9	Osmium.....	Os	190.9
Bromine.....	Br	79.92	<b>Oxygen.....</b>	<b>O</b>	<b>16.00</b>
Cadmium.....	Cd	112.40	Palladium.....	Pd	106.7
Cæsium.....	Cs	132.81	Phosphorus.....	P	31.04
Calcium.....	Ca	40.07	Platinum.....	Pt	195.2
Carbon.....	C	12.005	Potassium (Kalium)...	K	39.10
Cerium.....	Ce	140.25	Praseodymium.....	Pr	140.9
Chlorine.....	Cl	35.46	Radium.....	Ra	226.0
Chromium.....	Cr	52.0	Rhodium.....	Rh	102.9
Cobalt.....	Co	58.97	Rubidium.....	Rb	85.45
Columbium (Niobium)	Cb	93.1	Ruthenium.....	Ru	101.7
Copper (Cuprum)...	Cu	63.57	Samarium.....	Sa	150.4
Dysprosium.....	Dy	162.5	Scandium.....	Sc	44.1
Erbium.....	Er	167.7	Selenium.....	Se	79.2
Europium.....	Eu	152.0	Silicon.....	Si	28.3
Fluorine.....	F	19.0	Silver (Argentum)...	Ag	107.88
Gadolinium.....	Gd	157.3	Sodium (Natrium)...	Na	23.00
Gallium.....	Ga	70.1	Strontium.....	Sr	87.63
Germanium.....	Ge	72.5	Sulphur.....	S	32.06
Glucinum (Beryllium)	Gl	9.1	Tantalum.....	Ta	181.5
Gold (Aurum).....	Au	197.2	Tellurium.....	Te	127.5
Helium.....	He	4.00	Terbium.....	Tb	159.2
Holmium.....	Ho	163.5	Thallium.....	Tl	204.0
Hydrogen.....	H	1.008	Thorium.....	Th	232.15
Indium.....	In	114.8	Thulium.....	Tm	168.5
Iodine.....	I	126.92	Tin (Stannum).....	Sn	118.7
Iridium.....	Ir	193.1	Titanium.....	Ti	48.1
Iron (Ferrum).....	Fe	55.84	Tungsten (Wolfram- ium).....	W	184.0
Krypton.....	Kr	82.92	Uranium.....	U	238.2
Lanthanum.....	La	139.0	Vanadium.....	V	51.0
Lead (Plumbum)...	Pb	207.20	Xenon.....	Xe	130.2
Lithium.....	Li	6.94	Ytterbium (Neoytter- bium).....	Yb	173.5
Lutecium.....	Lu	175.0	Yttrium.....	Y	89.33
Magnesium.....	Mg	24.32	Zinc.....	Zn	65.37
Manganese.....	Mn	54.93	Zirconium.....	Zr	90.6
Mercury (Hydrar- gyrum).....	Hg	200.6			

# AN INTRODUCTION TO THE ANALYTICAL CHEMISTRY OF THE RARER ELEMENTS

## PREPARATION OF REAGENTS

### CONCENTRATED ACIDS

**Conc. HCl.** 12N. Sp. gr. 1.19 contains about 38 per cent HCl by weight.

**Conc. HNO<sub>3</sub>.** 16N. Sp. gr. 1.42 contains about 70 per cent HNO<sub>3</sub> by weight.

**Conc. H<sub>2</sub>SO<sub>4</sub>.** 36N. Sp. gr. 1.84 contains about 96 per cent H<sub>2</sub>SO<sub>4</sub> by weight.

**Conc. HF,** contains about 48 per cent HF.

**H<sub>2</sub>SO<sub>3</sub>.** A saturated aqueous solution of SO<sub>2</sub> at 15° contains about 16.5 per cent H<sub>2</sub>SO<sub>3</sub>.

### DILUTE ACIDS

**Dilute HCl.** 3N. Mix 25 cc. conc. HCl with sufficient water to make the volume 100 cc.

**Dilute HNO<sub>3</sub>.** 3N. Mix 19 cc. conc. HNO<sub>3</sub> with sufficient water to make the volume 100 cc.

**Dilute H<sub>2</sub>SO<sub>4</sub>.** 3N. In a beaker containing 80 cc. of distilled water, add with constant stirring 8.3 cc. of conc. H<sub>2</sub>SO<sub>4</sub>. Cool the solution to room temperature and then add sufficient water to make volume 100 cc.

**Tartaric Acid.** Make a saturated aqueous solution.

**Oxalic Acid.** H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O. 2N. 126 g. per liter.

### BASES

**Conc. NH<sub>4</sub>OH.** 15N. Sp. Gr. 0.90 contains about 28 per cent NH<sub>3</sub>.

**Dilute NH<sub>4</sub>OH.** 3N. Dilute 20 cc. of conc. NH<sub>4</sub>OH with 80 cc. of water.



**Sodium Hydroxide.** 6N. Use only NaOH purified by alcohol or reagent NaOH. This grade contains about 4 per cent of water. Hence the amount necessary to make 100 cc. will be  $6 \times \frac{40}{100} \times \frac{100}{96} = 25$  g. Dissolve this quantity of NaOH in 80 cc. of water, cool the solution and then add sufficient water to make the volume 100 cc. Filter through cotton if the solution is not perfectly clear.

### SOLUTIONS AND LIQUID REAGENTS

**Alcohol Ethyl.**  $C_2H_5OH$ . 95 per cent by volume.

**Alcohol Methyl.**  $CH_3OH$ .

**Ammonium Acetate.**  $NH_4C_2H_3O_2$ . 3N. 250 g. per liter.

**Ammonium Carbonate.**  $(NH_4)_2CO_3$ . Saturated aqueous solution.

**Ammonium Chloride.**  $NH_4Cl$ . Saturated aqueous solution.

**Ammonium Oxalate.**  $(NH_4)_2C_2O_4 \cdot H_2O$ . Saturated aqueous solution.

**Ammonium Sulphide** (colorless).  $(NH_4)_2S$ . Saturate 100 cc. of conc.  $NH_4OH$  with  $H_2S$  and add 100 cc. of conc.  $NH_4OH$ . Dilute the solution with 300 cc. of water.

**Ammonium Polysulphide.**  $(NH_4)_2S_x$ . Digest the colorless undiluted  $(NH_4)_2S$  with flowers of sulphur in the proportion of 1 gram to the liter and then dilute the solution with an equal volume of water.

**Antimony Trichloride.**  $SbCl_3$ . Dissolve 18.8 g. in 100 cc.  $HCl$  (1 : 1).

**Barium Chloride.**  $BaCl_2 \cdot 2H_2O$ . N. 122 g. per liter.

**Bromine Water.** A saturated aqueous solution.

**Cupferron.** 6 per cent aqueous solution.

**Dimethylglyoxime.** Treat 1 g. with 100 cc. 95 per cent alcohol. Heat to hasten solution.

**Formaldehyde.**  $HCHO$ . 40 per cent aqueous solution.

**Hydrochlorplatinic Acid.**  $H_2PtCl_6 \cdot 6H_2O$ . 10 per cent solution.

**Hydrogen Dioxide.** 3 per cent solution.

**Hydrogen Dioxide.** 30 per cent solution.

**Magnesia Mixture.** Dissolve 110 g.  $MgCl_2 \cdot 6H_2O$  and 280 g.  $NH_4Cl$  in 1 liter of distilled water; when solution is complete, add 261 cc. of  $NH_4OH$  (Sp. gr. 0.90), then add enough water to make the volume 2 liters.

**Mercuric Cyanide.**  $Hg(CN)_2$ . N. 126 g. per liter.

**Metanitrobenzoic Acid.** 0.4 g. in 100 cc.

**Potassium Bromide.** KBr. 0.5N. 60 g. per liter.

**Potassium Chromate.**  $K_2CrO_4$ . N. 97 g. per liter.

**Potassium Ferrocyanide.**  $K_4Fe(CN)_6 \cdot 3H_2O$ . N. 105 g. per liter.

**Potassium Fluoride.** KF. 3N. 174 g. per liter.

**Potassium Iodide.** KI. 0.5N. 83 g. per liter.

**Potassium Nitrite.**  $KNO_2$ . 500 g. per liter.

**Potassium Sulphate.**  $K_2SO_4$ . Saturated aqueous solution.

**Potassium Sulphide.**  $K_2S$ . 0.5N. 27.6 g. per liter.

**Potassium Thiocyanate.** KCNS. N. 97 g. per liter.

**Sodium Carbonate.** 3N. 159 g. per liter.

**Sodium Cobaltic Nitrite.**  $Na_3Co(NO_2)_6$ . Dissolve 100 g. of  $NaNO_2$  in 300 cc. of distilled water. Slightly acidify the solution with acetic acid and then add 10 g. of  $Co(NO_3)_2 \cdot 6H_2O$ . Allow the solution to stand for 24 hours and filter if necessary.

**Sodium Phosphate.**  $Na_2HPO_4 \cdot 12H_2O$ . N. 119 g. per liter.

**Stannic Chloride.**  $SnCl_4 \cdot 5H_2O$ . 29.5 g. in 100 cc.

**Stannous Chloride.** 0.5N in 3N·HCl. Dissolve 5.7 g. of  $SnCl_2 \cdot H_2O$  in 25 cc. of conc. HCl. Stir and heat if necessary till solution is complete. Add sufficient water to make the volume 100 cc. To prevent the solution from oxidizing keep the solution in a glass-stoppered bottle containing a strip of pure tin foil.

**Turmeric Solution.** Saturate 95 per cent ethyl alcohol with turmeric powder and filter the mixture.

#### REAGENTS IN SOLID FORM

**Ammonium Chloride.**  $NH_4Cl$ .

**Ammonium Persulphate.**  $(NH_4)_2S_2O_8$ .

**Asbestos Paper.**

**Ferrous Sulphate.**  $FeSO_4 \cdot 7H_2O$ . C.P. fine crystals.

**Lead Dioxide.**  $PbO_2$  free from Mn.

**Litmus Paper.** Blue and red, to be kept in stoppered tubes.

**Potassium Chloride.** KCl. C.P. fine crystals.

**Potassium Carbonate.**  $K_2CO_3$ . Anhydrous C.P.

**Sodium Bismuthate.**  $NaBiO_3$ .

**Sodium Carbonate.**  $Na_2CO_3$ . Anhydrous C.P.

**Sodium Formate.**  $NaHCO_2$ .

**Sodium Peroxide.**  $Na_2O_2$ . Pure.

**Sodium Sulphite.**  $Na_2SO_3$ . Anhydrous.

Sodium Thiosulphate.  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ .Thiourea.  $\text{CS}(\text{NH}_2)_2$ .

Zinc. Zn.

TABLE GIVING DATA FOR THE PREPARATION OF TEST SOLUTIONS OF KNOWN STRENGTH.

Group.	Metal.	Compound.	Formula Weight.	Solubility in 100 Parts of Water.	Per Cent Metal.	Quant. to Yield 100 mg. of Metal.
1	Tl	$\text{TlNO}_3$	266.01	$10^\circ$	76.65	0.130 g.
	W	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	330.	$41^\circ$	55.75	0.180
2A	Pd	$\text{PdCl}_2$	177.7	Sol. in HCl	60	0.167
	Rh	$\text{RhCl}_3 \cdot 4\text{H}_2\text{O}$	281.34	v.s.	36.6	0.274
	Ru	$\text{K}_2\text{RuCl}_5$	357.2	s.	28.5	0.352
	Os	$\text{OsO}_4$	254.9	s.	75	0.133
2B	Pt	$\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$	517.87	v.s.	37.7	0.265
	Ir	$\text{IrCl}_4$	334.94	s.	57.6	0.176
	Au	$\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$	412.11	v.s.	47.8	0.210
	Se(ous)	$\text{H}_2\text{SeO}_3$	129.22	v.s.	61.5	0.162
	Se(ic)	$\text{K}_2\text{SeO}_4$	221.40	$115^\circ$	35.8	0.280
	Te(ous)	$\text{K}_2\text{TeO}_3$	253.7	s.	50.3	0.198
	Te(ic)	$\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$	229.55	s.	55.5	0.180
	Mo	$\text{MoO}_3$	144	.....	66.6	0.150
3A	Be	$\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$	177.22	$100^{14}$	5.14	1.950
	Ti	$\text{TiO}_2 \cdot \text{H}_2\text{O}$	80.10	.....	49	0.204
	Th	$\text{Th}(\text{NO}_3)_4 \cdot 12\text{H}_2\text{O}$	696.67	v.s.	33.40	0.300
	Zr	$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$	321.65	v.s.	28.2	0.355
	Cb	$\text{Cb}_2\text{O}_5$	267	.....	70	0.144
	Ta	$\text{Ta}_2\text{O}_5$	443	.....	82	0.122
	U	$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	502.32	200	47.48	0.210
	Ce	$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	435.24	v.s.	32.28	0.310
	La	$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	433.13	v.s.	32.09	0.312
	Pr	$\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	435	s.	32.35	0.310
	Nd	$\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	438.42	v.s.	32.91	0.310
	Y	$\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	382.83	v.s.	23.2	0.430
	Er	$\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	461.53	s.	36.26	0.275
3B	V	$\text{NaVO}_3$	122	s.	41.8	0.239
5	Li	$\text{LiCl}$	42.40	$63^\circ$	16.42	0.610
	Rb	$\text{RbCl}$	120.91	$76^{10}$	70.68	0.142
	Cs	$\text{CsNO}_3$	194.82	$9.3^\circ$	68.17	0.146

## THE ANALYTICAL CLASSIFICATION OF THE RARER ELEMENTS

In the following table the rarer elements have been divided into five groups in accordance with their behavior towards the usual group reagents employed in systematic qualitative analysis.

Group 1.	Group 2.	Group 3.	Group 4.	Group 5.
Thallium Tungsten	<b>Division A</b> Ruthenium Rhodium Palladium Osmium (Thallium) <b>Division B</b> Platinum Iridium Gold Selenium Tellurium Molybdenum Germanium	<b>Division A</b> Beryllium Titanium Thorium Zirconium Columbium Tantalum Uranium Indium Gallium Cerium Lanthanum Praseodymium Neodymium Samarium Yttrium Erbium Scandium <b>Division B</b> Vanadium	Radium	Lithium Rubidium Caesium

### Group 1

The precipitate produced by HCl consists of  $\text{TiCl}$  and  $\text{H}_2\text{WO}_3$ . Molybdic, columbic and tantalic acids may also precipitate in this group, but they dissolve when an excess of HCl is added.  $\text{TiCl}$  like  $\text{PbCl}_2$  is slightly soluble in water and hence some passes into Group 2.



### Group 2

The composition of the sulphides of the rarer elements which are precipitated by  $\text{H}_2\text{S}$  from 0.3N HCl solution is shown below. The sulphides have been divided into two sub groups in accordance with their behavior towards  $(\text{NH}_4)_2\text{S}_x$ .

**Group 2. Division A. Sulphides Insoluble in  $(\text{NH}_4)_2\text{S}_x$ .**

$\text{Ru}_2\text{S}_3$ ,  $\text{Rh}_2\text{S}_3$ ,  $\text{PdS}$ ,  $\text{OsS}_4$  ( $\text{Ti}_2\text{S}$ ).

**Group 2. Division B. Sulphides Soluble in  $(\text{NH}_4)_2\text{S}_x$ ,**

$\text{PtS}_2$ ,  $\text{Ir}_2\text{S}_3$ ,  $\text{AuS}$ ,  $\text{Se}+\text{S}$ ,  $\text{TeS}_2$ ,  $\text{MoS}_3$ ,  $\text{GeS}_2$ .

Gold and platinum are usually found in both divisions, the amounts depending upon the relative quantities of the other metals of Division B which are present. In the absence of other metals of 2B,  $\text{PtS}_2$  dissolves only slightly in  $(\text{NH}_4)_2\text{S}_x$ . When molybdenum is present in amounts equal to or greater than 50 mg., a moderate quantity remains in the residue after extraction with  $(\text{NH}_4)_2\text{S}_x$ . The amount which goes into solution under these conditions is sufficient however, to make its detection certain in 2B, while the undissolved portion does not interfere with the detection of the 2A metals. While thallium is not precipitated by  $\text{H}_2\text{S}$  in acid solution, it occasionally comes down in combination with the sulphide of arsenic or antimony. On treating this precipitate with  $(\text{NH}_4)_2\text{S}_x$ ,  $\text{Ti}_2\text{S}$  is left in the residue; hence its inclusion in 2A.

Tungsten and vanadium are not directly precipitated by  $\text{H}_2\text{S}$  in acid solution and hence strictly do not belong to this group. If, however, the original solution containing these metals is treated with  $(\text{NH}_4)_2\text{S}_x$  and then acidified with HCl,  $\text{WS}_3$  and  $\text{V}_2\text{S}_5$  will be thrown down. It is because these sulphides, when once formed, are insoluble in dilute HCl, that some writers include W and V in Group 2. Moreover, if the original substance is decomposed by fusion with a mixture of  $\text{Na}_2\text{CO}_3$  and S, the aqueous extract of the melt will contain W and V together with the common metals of 2B as thio salts. On acidifying this solution,  $\text{WS}_3$  and  $\text{V}_2\text{S}_5$  will be precipitated along with the sulphides of As, Sb and Sn. It is important to remember when one of the above procedures is followed, that NiS and CoS will also be found with the sulphides of 2A. In systematic analysis, tungsten would be precipitated in



Group 1, while vanadium would remain in solution until the filtrate from Group 3 was acidified with HCl, when  $V_2S_5$  would come down.

### Group 3

The composition of the Group 3 precipitate is shown below:

#### Group 3A

$Be(OH)_2$ ,  $Ti(OH)_4$ ,  $Th(OH)_4$ ,  $Zr(OH)_4$ ,  $H_3CbO_4$ ,  $H_3TaO_4$   
 $Ce(OH)_3$ ,  $La(OH)_3$ ,  $Pr(OH)_3$ ,  $Nd(OH)_3$ ,  $Sa(OH)_3$ ,  $Y(OH)_3$ ,  
 $Er(OH)_3$ ,  $Sc(OH)_3$ ,  $(UO_2)_3S$ ,  $Ga_2S_3$ ,  $In_2S_3$ .

#### Group 3B



The following elements also belong to Group 3; europium, gadolinium, terbium, dysprosium, holmium, ytterbium, and lutecium. They have not been included, because of their extreme rarity. As stated above, vanadium does not come down in Group 3. When, however, the filtrate from Group 3 is acidified with HCl,  $V_2S_5$  is precipitated. For this reason it has seemed proper to place this element in a separate sub-division.

### Group 4

The extremely rare and costly element radium (Ra) belongs to this group. If present it will be precipitated as a carbonate along with Ba, Sr, and Ca.

### Group 5

This group comprises those metals which are not precipitated by any of the group reagents. Of the rarer elements belonging to this group, caesium and rubidium show a striking resemblance to potassium and ammonium in their chemical relationships. Lithium resembles the alkaline earth metals in forming an insoluble phosphate and a difficultly soluble carbonate.

## GROUP 1. THALLIUM (Tl) AND TUNGSTEN (W)

## THALLIUM

In the following experiments, use a solution of thallous nitrate of strength 5 mg. Tl per cubic centimeter.

1. **Action of HCl and Properties of TlCl.** To 1 cc. of  $\text{TlNO}_3$  solution contained in a test-tube, add dil. HCl drop by drop until no further precipitation takes place. Note the color and nature of the precipitate. Write the equation for the reaction. Shake the mixture to coagulate the precipitate and allow it to settle. Carefully decant the clear solution. To the precipitate in the test-tube add 5 cc. of water and boil. Note that the precipitate dissolves. Divide the solution into two equal portions. To one add a few drops of dilute  $\text{H}_2\text{SO}_4$ . Note that no precipitate forms (distinction from Pb). To the other portion add a few drops of  $\text{K}_2\text{CrO}_4$  solution. The yellow precipitate is  $\text{Tl}_2\text{CrO}_4$ . How would you distinguish Pb from Tl? How does the solubility of TlCl compare with that of  $\text{PbCl}_2$ ?

2. **Action of KI.** Treat 1 cc. of  $\text{TlNO}_3$  solution with 2 or 3 drops of KI solution. The yellow precipitate which forms is  $\text{TlI}$ .

3. **Action of KBr.** Repeat Exp. 2 using a dilute solution of KBr instead of KI.

4. **Action of  $\text{H}_2\text{PtCl}_6$ .** By means of a pipette introduce on a small watch-glass three drops of  $\text{TlNO}_3$  solution. Add one drop of 10 per cent  $\text{H}_2\text{PtCl}_6$ . The precipitate is  $\text{Tl}_2\text{PtCl}_6$ .

5. **Action of  $\text{Na}_3\text{Co}(\text{NO}_2)_6$ .** Add a few drops of  $\text{Na}_3\text{Co}(\text{NO}_2)_6$  solution to 1 cc. of  $\text{TlNO}_3$  solution. The precipitate is  $\text{Tl}_3\text{Co}(\text{NO}_2)_6$ .

6. **Action of  $\text{K}_2\text{CrO}_4$ .** That thallous salts are precipitated by  $\text{K}_2\text{CrO}_4$  has been shown in Exp. 1. The precipitate is insoluble in dilute  $\text{HNO}_3$  and in dilute  $\text{H}_2\text{SO}_4$ .

7. **Action of  $(\text{NH}_4)_2\text{S}$ .** In a test-tube treat 1 cc. of  $\text{TlNO}_3$  solution with a few drops of  $(\text{NH}_4)_2\text{S}$ . The black precipitate which forms is  $\text{Tl}_2\text{S}$ .

8. **Action of  $\text{H}_2\text{S}$ .** In a small beaker dilute 2 cc. of  $\text{TlNO}_3$  solution with 20.5 cc. of water. Add 2.5 cc. dil. HCl (3N). The resulting solution the volume of which will be 25 cc., will have the

proper hydrogen ion concentration for the precipitation of the Group 2 metals by  $\text{H}_2\text{S}$ . Pass  $\text{H}_2\text{S}$  into the solution. Note that  $\text{H}_2\text{S}$  does not precipitate Tl under these conditions. If all the Tl is not precipitated in Group 1, where will it again appear in the course of systematic analysis? (See Exp. 7.) Divide the solution which has been treated with  $\text{H}_2\text{S}$  into two equal portions. To one, in a test-tube, add 1 g. of  $\text{NaC}_2\text{H}_3\text{O}_2$  and shake the mixture. To the other portion add dil.  $\text{NH}_4\text{OH}$  to alkaline reaction. Note and explain the formation of  $\text{Tl}_2\text{S}$  in each case.

**9. Action of NaOH, KOH or  $\text{NH}_4\text{OH}$ .** (a) To a few drops of  $\text{TlNO}_3$  solution on a small watch glass, add a few drops of NaOH solution. Note that no precipitate forms. (b) Repeat experiment (a) using a few drops of dil.  $\text{NH}_4\text{OH}$  instead of NaOH.

**10. Oxidation of Thallous to Thallie Salts.** Introduce into a test-tube 3 cc. of  $\text{TlNO}_3$  solution. Add 2 cc. dil.  $\text{H}_2\text{SO}_4$  and 0.5 g  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ . Boil the solution for 2 or 3 minutes and then cool it thoroughly. Divide the solution into 3 equal portions. To the first, add a few drops of dil. HCl. Note that no precipitate forms (absence of Tl(ous)). Make the second portion alkaline with dil  $\text{NH}_4\text{OH}$ . The brown precipitate which forms is  $\text{Tl}(\text{OH})_3$  (presence of Tl(ic)). Treat the third portion with a few drops of  $\text{SnCl}_2$  solution. The white precipitate is  $\text{TlCl}$ , which precipitates because of the reduction of thallie to thallous ions by the  $\text{SnCl}_2$ .

**Note.** Chlorides and chromates do not precipitate thallie ions.

**11. Flame and Spectroscopic Tests for Thallium.** Place a few drops of  $\text{TlNO}_3$  solution on a small watch glass. Moisten end of a platinum wire with this solution and hold it in the flame. Observe the green color of the flame. Examine the green flame with a spectroscope and note the green line.

## TUNGSTEN

Use a solution of  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  of strength 10 mg. W per cubic centimeter.

**1. (a) Action of Mineral Acids.** To 1 cc. of  $\text{Na}_2\text{WO}_4$  solution add 1 cc. of dil. HCl and shake the mixture for a few moments. The white amorphous precipitate which separates is hydrated tungstic acid  $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$ . Heat the mixture to boiling and note that the precipitate becomes yellow due to the formation



of anhydrous tungstic acid  $\text{H}_2\text{WO}_4$ . **Note.**  $\text{H}_2\text{WO}_4$  may also be precipitated by  $\text{HNO}_3$  or  $\text{H}_2\text{SO}_4$ .

(b) **Influence of Tartaric Acid on the Precipitation of  $\text{H}_2\text{WO}_4$ .** In a test-tube treat 2 cc. of  $\text{Na}_2\text{WO}_4$  solution with 2 cc. of a saturated solution of  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ . Now add 1 cc. of dil.  $\text{HCl}$  and heat. Note that precipitation does not take place.

**Note.** From solutions of metatungstates, mineral acids do not precipitate  $\text{H}_2\text{WO}_4$ . However, on prolonged boiling in the presence of an excess of acid, the soluble metatungstic acid is changed to the ortho form, which then precipitates.

**2. Action of  $\text{H}_2\text{S}$ .** Introduce into a small beaker 1 cc. of  $\text{Na}_2\text{WO}_4$  solution. Add 21.5 cc. of water and 2.5 cc. dil.  $\text{HCl}$ . Mix and treat with  $\text{H}_2\text{S}$ . Note result.

**3. Action of  $(\text{NH}_4)_2\text{S}_x$  and the Formation of  $\text{WS}_3$ .** To 2 cc. of  $\text{Na}_2\text{WO}_4$  solution contained in a test-tube, add 2 drops of conc.  $\text{NH}_4\text{OH}$  and treat the resulting solution with  $\text{H}_2\text{S}$ . Note that no precipitate forms but that the solution becomes yellow. Now acidify the solution with dil.  $\text{HCl}$  and observe that a brown precipitate forms. This is  $\text{WS}_3$ . Heat the mixture to coagulate the precipitate, filter and wash the precipitate twice with hot water. To the  $\text{WS}_3$  on the filter, add 2 cc. of  $(\text{NH}_4)_2\text{S}_x$  and catch the solution in a test-tube. Observe that  $\text{WS}_3$  dissolves in  $(\text{NH}_4)_2\text{S}_x$ . Acidify the filtrate with dil.  $\text{HCl}$  and note again the precipitation of  $\text{WS}_3$ . If all the tungsten is not precipitated in Group 1, where will it again appear in the course of systematic analysis?

**4. Action of  $\text{SnCl}_2$ .** Introduce into a test-tube 2 drops of  $\text{Na}_2\text{WO}_4$  solution. Add 1 or 2 drops of  $\text{SnCl}_2$  solution and note the pale yellow precipitate which results. Now add 2 cc. of conc.  $\text{HCl}$  and shake the mixture. Observe the formation of a beautiful blue coloration. If instead of 2 drops, 0.5 cc. of the tungstate solution is used, a blue precipitate instead of a solution will be obtained.

**5. Action of  $\text{Zn}$  and  $\text{HCl}$ .** To 1 cc. of  $\text{Na}_2\text{WO}_4$  solution add 2 cc. of conc.  $\text{HCl}$  and a small piece of  $\text{Zn}$ . Observe that the tungstic acid which is first precipitated rapidly becomes blue (due to the formation of  $\text{W}_2\text{O}_5$ ).

## GROUP 2

**Division A.** Ru, Rh, Pd, Os.

**Division B.** Au, Pt, Ir, Se, Te, Mo.

## RUTHENIUM

Use a solution of  $\text{K}_2\text{RuCl}_5$  (potassium pentachlororuthenate) of strength 1 mg. Ru per cubic centimeter. It is best to add a little dil. HCl. to the water in which the crystals of  $\text{K}_2\text{RuCl}_5$  are dissolved. A solution of  $\text{RuCl}_3$  containing some HCl may also be used for the following experiments.

1. **Action of  $\text{H}_2\text{S}$ .** Introduce 5 cc. of  $\text{K}_2\text{RuCl}_5$  solution into a small beaker. Add 2.5 cc. dil. HCl and dilute the solution with water to 25 cc. Pass in  $\text{H}_2\text{S}$ . Heat the solution to boiling and again treat with  $\text{H}_2\text{S}$  for several minutes. The black precipitate which forms after some time is  $\text{Ru}_2\text{S}_3$ . Filter off the precipitate and wash it with 10 cc. of hot water. Puncture the filter and wash contents into a test-tube with the aid of 10 cc. of water. Boil the mixture, allow the precipitate to settle and carefully pour off most of the clear solution. Divide the residual mixture in the test-tube into two equal portions. To one portion add 1 cc. of  $(\text{NH}_4)_2\text{S}_x$  and warm the mixture. Note that solution does not completely take place. To the other portion add an equal volume of conc.  $\text{HNO}_3$ . Boil and note that the precipitate completely dissolves.

2. **Action of  $(\text{NH}_4)_2\text{S}$ .** To 1 cc. of ruthenium solution add 1 cc. of dil.  $\text{NH}_4\text{OH}$ . Pass in  $\text{H}_2\text{S}$  for about thirty seconds. Heat to boiling and again treat with  $\text{H}_2\text{S}$ . Shake the mixture. The black precipitate is  $\text{Ru}_2\text{S}_3$ .

3. **Action of NaOH.** Treat 1 cc. of ruthenium solution with five drops of NaOH. Boil the solution and allow it to settle. The black precipitate which forms is  $\text{Ru}(\text{OH})_3$ .

4. **Action of Zn.** Introduce into a small evaporating dish 2 cc. of ruthenium solution and 1 cc. of conc. HCl. Add a small piece of Zn. Note that the solution becomes indigo blue in color and that finally metallic Ru separates.

5. **Action of KCNS.** To 1 cc. of ruthenium solution add 1 cc. of KCNS. Heat and note the changes in color of the solution which is first red, then purple and finally violet.



6. **Glow Test of Curtman and Rothberg.** Apply the glow test (see Exp. 11, under *Platinum*) to a few drops of ruthenium solution. Note that the test is negative (distinction from all the other platinum metals except Os).

7. **Action of  $\text{Na}_2\text{S}_2\text{O}_3$ .** Introduce into a test-tube 0.2 g.  $\text{Na}_2\text{S}_2\text{O}_3$  and 1 cc. of dil.  $\text{NH}_4\text{OH}$ . Shake the mixture till solution is complete. Now add 2 drops of ruthenium solution and heat to boiling. Note the reddish-purple color. **Note.** This test is capable of detecting Ru in the presence of a large excess of Ir.

8. **Action of  $\text{KNO}_2$ , etc.** To 1 cc. of ruthenium solution in a small evaporating dish, add  $\text{Na}_2\text{CO}_3$  solution drop by drop with stirring until the solution is alkaline to litmus. Add 3 drops of  $\text{KNO}_2$  solution and boil the mixture. Transfer the contents of the evaporating dish to a test-tube and hold the tube under running cold water from the tap until it is thoroughly cool. Now add 2 drops (no more) of freshly prepared colorless  $(\text{NH}_4)_2\text{S}$  (prepared by passing  $\text{H}_2\text{S}$  for 30 seconds into 2 cc. of dil.  $\text{NH}_4\text{OH}$  contained in a test-tube). Note the red color which develops in the tube and which on standing changes to brown.

## RHODIUM

Use a solution of  $\text{RhCl}_3$  containing 1 mg. Rh per cubic centimeter.

1. **Action of  $\text{H}_2\text{S}$  and Properties of  $\text{Rh}_2\text{S}_3$ .** Introduce into a small beaker 10 cc. of rhodium solution. Add 2.5 cc. dil.  $\text{HCl}$  and dilute the solution with water to 25 cc. Heat to boiling and pass in  $\text{H}_2\text{S}$  for about 30 seconds. Observe that little or no precipitation takes place. Heat to boiling and again pass in  $\text{H}_2\text{S}$  for about a half minute. Repeat this process of boiling and treating with  $\text{H}_2\text{S}$  till precipitation seems complete. The dark brown precipitate is  $\text{Rh}_2\text{S}_3$ . Filter on a small filter and wash the precipitate with 10 cc. of hot water. Pierce the apex of the filter with a platinum wire and wash contents of filter into a test-tube with the aid of a forceful stream of water from a wash bottle using about 10 cc. Heat the mixture in the test-tube to boiling and allow the precipitate to settle. Pour off most of the water. Shake the suspended precipitate remaining in the test-tube and divide it into three equal portions. In a test-tube, treat the first portion with 2 cc. conc.  $\text{HNO}_3$  and boil for one minute.

Notice that the precipitate dissolves with difficulty. To the second portion add 1 cc. of  $(\text{NH}_4)_2\text{S}_x$  and heat. Note that the precipitate does not dissolve. Treat the third portion in a test-tube with 3 cc. of dil. aqua regia and boil for one minute. Note that complete solution takes place.

2. **Action of NaOH.** To 1 cc. of rhodium solution add 1 drop of NaOH and 2 drops of ethyl alcohol. Heat to boiling, shake and allow to settle. The brownish-black precipitate is  $\text{Rh}(\text{OH})_3$ .

3. **Action of  $\text{KNO}_2$ .** In a test-tube treat 2 cc. of rhodium solution with 1 cc. of  $\text{KNO}_2$  solution. Heat to boiling, shake the mixture and allow the tube to stand for one minute. The slowly forming yellow precipitate is  $\text{K}_3\text{Rh}(\text{NO}_2)_6$ . Set the tube aside for from five to ten minutes and examine again the precipitate which has settled.

4. **Action of Sodium Formate.** To 1 cc. of rhodium solution add 0.2 g. sodium formate. Heat the solution to boiling. The black precipitate is metallic Rh. **Note.** Zn also reduces rhodium solutions.

5. **Glow Test.** Absorb a few drops of rhodium solution in a piece of thin asbestos paper and carry out the test in the manner described in Exp. 11 under Pt.

## PALLADIUM

Use a solution of  $\text{PdCl}_2$  of strength 1 mg. Pd per cubic centimeter. The solution should contain about 1 cc. of conc. HCl in every 50 cc. of solution.

1. **Action of  $\text{H}_2\text{S}$ .** Introduce into a small beaker 10 cc. of palladium solution. Add 2.5 cc. dil. HCl and dilute the solution with water to 25 cc. Heat to boiling and pass in  $\text{H}_2\text{S}$ . The black precipitate is PdS. Heat the mixture to boiling and allow the precipitate to settle. Pour off the clear solution. Add 25 cc. of water to the precipitate in the beaker, boil, allow to settle and pour off most of the water. Use small portions of the residual mixture of water and PdS to determine the solubilities of PdS in the following: (a) **Aqua Regia.** In a test-tube add to a little of the mixture, 3 cc. of dilute aqua regia. Boil for about a minute and note that the PdS completely dissolves. (b) **Dilute  $\text{HNO}_3$ .** To a small portion of the PdS suspension, add 2 cc. dil.  $\text{HNO}_3$  and

boil. Observe that the precipitate does not dissolve. (c)  $(\text{NH}_4)_2\text{S}_x$ . To another portion of the PdS precipitate add 2 cc.  $(\text{NH}_4)_2\text{S}_x$  and warm the mixture. Note that the precipitate does not dissolve.

2. **Action of KI.** To 2 drops of palladium solution add 1 drop of KI solution. The black precipitate which forms is  $\text{PdI}_2$ . Now add 3 cc. of KI solution in excess and note that the precipitate dissolves yielding a brownish-red solution.

3. **Action of NaOH.** In a test-tube heat to boiling 1 cc. of palladium solution. Add from a medicine dropper just one drop of NaOH solution and shake the mixture. The brown precipitate is a basic salt.

4. **Action of  $\text{NH}_4\text{OH}$ .** To 1 cc. of palladium solution containing 2 mg. of Pd, add 1 drop of dil.  $\text{NH}_4\text{OH}$  and shake the solution about a dozen times. Now add another drop of dil.  $\text{NH}_4\text{OH}$  and shake. Continue this process of adding  $\text{NH}_4\text{OH}$  and shaking until four or five drops of dil.  $\text{NH}_4\text{OH}$  have been added. The pink crystalline precipitate which forms is  $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ . To the precipitate in the test-tube add 2 cc. conc.  $\text{NH}_4\text{OH}$  and heat the tube to boiling. Note that the precipitate dissolves to a perfectly colorless solution.

5. **Action of Dimethylglyoxime.** To 1 cc. of palladium solution add 1 cc. of an alcoholic solution of dimethylglyoxime. Shake the tube and note the formation of a voluminous orange-yellow precipitate. Add 2 cc. of conc.  $\text{NH}_4\text{OH}$ , shake the mixture vigorously and note that the precipitate dissolves (distinction from Ni). **Note.** The precipitate is sparingly soluble in water, in 50 per cent. alcohol, and in dilute acids (method of separation of Pd from other platinum metals except Pt).

6. **Action of  $\text{NH}_4\text{Cl}$ .** On a small watch glass introduce by means of a medicine dropper, 1 drop of  $\text{PdCl}_2$  solution of strength 10 mg. Pd per cubic centimeter. Add 1 drop of a saturated aqueous solution of  $\text{NH}_4\text{Cl}$ . Stir the mixture and scratch the bottom of the watch glass with the stirrer. Observe that no precipitate forms. Now add 1 drop of conc.  $\text{HNO}_3$  and stir again. The red precipitate which forms is  $(\text{NH}_4)_2\text{PdCl}_6$ .

7. **Action of  $\text{Hg}(\text{CN})_2$ .** To 1 cc. of palladium solution add 1 cc. of  $\text{Hg}(\text{CN})_2$  solution. Shake the tube for about thirty seconds. The yellowish-white gelatinous precipitate which forms is  $\text{Pd}(\text{CN})_2$ . **Note.** On ignition the precipitate decomposes leaving a residue



of spongy Pd. By means of  $\text{Hg}(\text{CN})_2$ , palladium may be separated from all the other platinum metals.

### 8. Action of Reducing Agents.

(a) **Sodium Formate.** Treat 1 cc. of palladium solution in a test-tube with 0.2 g. sodium formate. Heat to boiling. The black precipitate is Pd.

(b) **Zn+HCl.** To 2 cc. of palladium solution, add 1 cc. of conc. HCl and a small piece of Zn. Note that the solution becomes colorless. After the action has been allowed to proceed for two minutes, shake the mixture and note the black flocculent particles of metallic Pd.

(c)  **$\text{FeSO}_4$ .** In a test-tube treat 1 cc. of palladium solution with 0.5 g.  $\text{FeSO}_4$ . Heat. Note the deposition of black Pd.

9. **Glow Test.** Apply the glow test to a few drops of palladium solution, following directions given in Exp. 11 under Platinum.

## OSMIUM

**Note.** Osmium tetroxide  $\text{OsO}_4$  is the most common compound of this element. When pure it consists of transparent water-white crystals. The product usually met with in commerce is yellow. It dissolves in water and imparts to the solution its characteristic odor resembling chlorine or ozone.  $\text{OsO}_4$  is readily volatile and is given off when any osmium compound is heated with  $\text{HNO}_3$ . If the vapors are absorbed in KOH, the latter acquires a yellow color due to the formation of potassium osmate  $\text{K}_2\text{OsO}_4$ .



Use an aqueous solution of  $\text{OsO}_4$  containing 1 mg. Os per cubic centimeter.

1. **Odor of Osmic Acid.** Note the odor of an aqueous solution of osmic acid.

2. **Action of  $\text{H}_2\text{S}$ .** Introduce into a small beaker 10 cc. of osmium solution. Add 2.5 cc. of dil. HCl and dilute the solution with water to 25 cc. Pass in  $\text{H}_2\text{S}$ . The black precipitate is  $\text{OsS}_4$ . Allow the precipitate to settle and pour off the clear solution. Add 10 cc. of water and boil the mixture. Allow the precipitate to settle and pour off the clear solution. Now add 1 cc. of  $(\text{NH}_4)_2\text{S}_x$  and heat gently. Observe that the precipitate does not dissolve.

3. **Action of NaOH on a Dilute Solution of  $\text{OsO}_4$ .** To 1 cc. of osmium solution add 1 drop of NaOH. Note the yellow color of the resulting solution.

4. **Action of Thiourea.** Treat 1 cc. of osmium solution in a test-tube with 2 drops of dil. HCl and one small crystal of thiourea. Shake the solution and note the red color.

5. **Action of Reducing Agents.**

(a) **Sodium Formate.** To 1 cc. of osmium solution add 0.2 g. sodium formate. Heat to boiling and note the reduction to metallic Os.

(b) **Sulphurous Acid.** To 2 cc. of osmium solution add 2 cc. of  $\text{H}_2\text{SO}_3$ . Heat to boiling and note the indigo-blue color which develops.

(c)  **$\text{SnCl}_2$ .** In a test-tube treat 1 cc. of osmium solution with 1 cc. of  $\text{SnCl}_2$ . Note brown coloration.

(d)  **$\text{FeSO}_4$ .** Treat 1 cc. of osmium solution contained in a test-tube with 0.2 g.  $\text{FeSO}_4$ . Shake the mixture vigorously. The black precipitate is  $\text{OsO}_2$ .

(e)  **$\text{Na}_2\text{S}_2\text{O}_3$ .** To 1 cc. of osmium solution add 0.2 g.  $\text{Na}_2\text{S}_2\text{O}_3$ . Shake the solution vigorously. The black precipitate is  $\text{OsS}_2$  mixed with S.

**Note.** Zn in the presence of strong mineral acids, precipitates metallic Os.

6. **Glow Test.** Apply the glow test (see Exp. 11 under Pt) to a few drops of  $\text{OsO}_4$  solution. Note that the test is negative (distinction from all the other platinum metals except Ru).

## PLATINUM

Use a solution of  $\text{H}_2\text{PtCl}_6$  of strength 1 mg. Pt per cubic centimeter in all the experiments in which the strength of the solution is not specified.

1. (a) **Precipitation and Properties of  $\text{PtS}_2$ .** Introduce into a small beaker 10 cc. of  $\text{H}_2\text{PtCl}_6$  solution. Add 2.5 cc. dil. HCl and dilute the solution with water to 25 cc. Pass in  $\text{H}_2\text{S}$  for several minutes and observe that the solution becomes yellow. **Note.** More concentrated solutions become brown due to the reduction of the  $\text{H}_2\text{PtCl}_6$ . Heat the solution to boiling and treat it with a stream of  $\text{H}_2\text{S}$  for one minute. Heat again to boiling and pass in  $\text{H}_2\text{S}$  for a few minutes. Filter the precipitate of  $\text{PtS}_2$  on a 6 cm.



filter paper and wash it five times with separate 5 cc. portions of boiling water. Test the last washings for chlorides with  $\text{AgNO}_3$  and if still present, continue the washing until a negative test is obtained. **Note.** Thorough washing of the precipitate is necessary in order to remove any adhering  $\text{HCl}$  which would vitiate the next test.

(b) **Action of Hot Dilute  $\text{HNO}_3$  and Aqua Regia on  $\text{PtS}_2$ .** Perforate the apex of the filter containing the  $\text{PtS}_2$  with a platinum wire and then enlarge the hole. With a stream of water from a wash bottle, wash down the precipitate through the apex and catch the mixture in a test-tube. Heat the mixture of  $\text{PtS}_2$  and water to boiling and allow the precipitate to settle. Carefully pour off the clear solution leaving about 1 cc. in the tube. Transfer one-half of the mixture of  $\text{PtS}_2$  and water to another test-tube and to the latter add 1 cc. of dil.  $\text{HNO}_3$ . Boil. Note that the precipitate does not dissolve. Now add 2 cc. of dil.  $\text{HCl}$  (forming aqua regia) and heat to boiling. Note that the precipitate dissolves.

(c) **Action of  $(\text{NH}_4)_2\text{S}_x$  on  $\text{PtS}_2$ .** To the other test-tube containing  $\text{PtS}_2$  add the small portion of the filter paper to which  $\text{PtS}_2$  adheres. Add 2 cc. of  $(\text{NH}_4)_2\text{S}_x$ , shake for several minutes and heat (do not boil). Filter on a 7 cm. filter and observe that the greater part of the  $\text{PtS}_2$  remains undissolved. Acidify the  $(\text{NH}_4)_2\text{S}_x$  filtrate with dil.  $\text{HCl}$ , heat to boiling and compare the precipitate with that obtained by acidifying in another test-tube 2 cc.  $(\text{NH}_4)_2\text{S}_x$  with dil.  $\text{HCl}$  and boiling the mixture. Allow both tubes to stand for fifteen to twenty minutes and compare the precipitates which settle at the bottoms of the tubes as to color. What can you say about the solubility of  $\text{PtS}_2$  in  $(\text{NH}_4)_2\text{S}_x$ ?

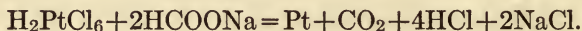
2. **Action of  $(\text{NH}_4)_2\text{S}$ .** In a test-tube treat 1 cc. of platinum solution with 1 cc. of dil.  $\text{NH}_4\text{OH}$ . Pass  $\text{H}_2\text{S}$  into the solution for a few moments. Shake and allow to stand. Observe the formation of a brown precipitate.

3. **Action of  $\text{KCl}$  or  $\text{NH}_4\text{Cl}$ .** Boil down in a test-tube 3 cc. of platinum solution to about 1 cc. Cool thoroughly under running cold water from the tap. Add 0.5 g.  $\text{KCl}$  and shake the mixture. The yellow precipitate is  $\text{K}_2\text{PtCl}_6$ . **Note.**  $\text{NH}_4$ ,  $\text{Cs}$ ,  $\text{Rb}$  and  $\text{Tl}$  form a similar salt under the same conditions.

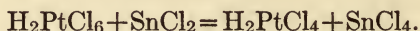
4. **Action of  $\text{FeSO}_4$ .** To 1 cc. of platinum solution add 1 cc. dil.  $\text{HCl}$  and 0.5 g.  $\text{FeSO}_4$ . Boil. Note that no precipitate forms (distinction from  $\text{Au}$ ).

**5. Action of  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{H}_2\text{SO}_3$ .** **Note.** Neither of these reagents precipitates platinum (distinction from Au). The student may verify these negative results if the supply of platinum solution is plentiful.

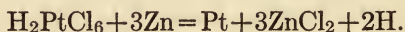
**6. Sodium Formate.** To 2 cc. of  $\text{H}_2\text{PtCl}_6$  solution containing 1 mg. Pt, add 0.1 g. sodium formate and heat the mixture to boiling. The black precipitate is metallic platinum. **Note.** When formic acid is used no precipitate is obtained until the solution is neutralized with  $\text{Na}_2\text{CO}_3$ .



**7. Action of  $\text{SnCl}_2$ .** To 2 cc. of  $\text{H}_2\text{PtCl}_6$  containing 1 mg. Pt, add 2 cc. of dil. HCl and 2 drops of  $\text{SnCl}_2$  solution. Shake the mixture and note the deep orange color which develops due to formation of hydrochlorplatinous acid.



**8. Action of  $\text{Zn} + \text{HCl}$ .** To 5 cc. of platinum solution add 3 cc. of conc. HCl and 0.5 g. granulated Zn. Allow the action to continue for a minute and note the black particles of metallic platinum which separate and which remain after all the Zn is dissolved.



**Note.** The same result can be brought about by using Cd, Mg, or Al instead of Zn.

**9. Action of KI.** In a test-tube treat 1 cc. of platinum solution containing 0.5 mg. Pt with 1 drop of KI solution. The dark-red coloration is due to the liberated iodine and the simultaneous reduction of hydrochlorplatinic acid.



**Note.** This is an exceedingly delicate test for Pt; but it is not quite as sensitive as the glow test of Curtman and Rothberg.

**10. Action of Formaldehyde.** **Note.** A 40 per cent aqueous solution of formaldehyde reduces alkaline platinum solutions giving a precipitate of finely divided platinum.

11. **The Glow Test of Curtman and Rothberg.** Pour on a small watch glass 0.5 cc. of  $\text{H}_2\text{PtCl}_6$  containing 0.5 mg. Pt per cubic centimeter. By means of a small piece of thin asbestos paper held by a pair of forceps, absorb a little of this solution and hold it in the flame until all the water has evaporated. Repeat this process of dipping and heating until the entire 0.5 cc. has been absorbed. Now heat the asbestos to redness. Turn off the gas and as soon as the flame is out, **quickly** turn on the gas and hold the asbestos, which should still be warm, in the path of the unlighted mixture of gas and air. Observe that the asbestos glows. If the glow is allowed to die out, it can be brought back again by heating the paper again and holding it in the stream of mixed gas and air. **Note.** By means of this test 0.002 mg. Pt can be detected. It serves also to detect Pd, Ir, and Rh. For further details concerning this test, see Jour. Amer. Chem. Soc. Vol. 33. (1911) pp. 718-724.

## IRIDIUM

Prepare a solution of  $\text{H}_2\text{IrCl}_6$  of strength 10 mg. Ir per cubic centimeter by dissolving the calculated amount (see Table) of  $\text{IrCl}_4$  in 20 cc. of water containing dil. HCl. Dilute separate portions of this solution with water to give solutions of strength 5, 2 and 1 mg. respectively of Ir per cubic centimeter.

1. **Action of  $\text{H}_2\text{S}$ .** Introduce into a small beaker 10 cc. of iridium solution containing 1 mg. Ir per cubic centimeter. Add 2.5 cc. of dil. HCl and dilute the solution with water to 25 cc. Pass in  $\text{H}_2\text{S}$ . Note the bleaching of the solution with the separation of sulphur. Heat the mixture to boiling and again treat with  $\text{H}_2\text{S}$  for about thirty seconds. Boil again and pass in  $\text{H}_2\text{S}$  for a half minute. Repeat this process of boiling and treating with  $\text{H}_2\text{S}$  until a brown precipitate is obtained. Its formula is  $\text{Ir}_2\text{S}_3$ . **Note.**  $\text{Ir}_2\text{S}_3$  is soluble in  $(\text{NH}_4)_2\text{S}_x$ .

2. **Action of  $\text{NH}_4\text{OH}$ .** In a test-tube treat 1 cc. of iridium solution containing 2 mg. Ir with 1 cc. of dil.  $\text{NH}_4\text{OH}$ . Note the change in color from brown to olive-green. **Note.** NaOH produces the same change in color.

3. **Action of  $(\text{NH}_4)_2\text{S}$ .** Treat in a test-tube 2 cc. of iridium solution containing 2 mg. of Ir per cubic centimeter with 2 cc. of dil.  $\text{NH}_4\text{OH}$ . Note the olive-green color of the solution. Pass in  $\text{H}_2\text{S}$  and observe that no precipitate forms, also that the solu-



tion assumes a darker color. Acidify the solution with dil. HCl. Note that the color is bleached. Heat the solution to boiling and observe the brown turbidity which is due to the separation of  $\text{Ir}_2\text{S}_3$ .

**4. Action of NaOH.** To 1 cc. of iridium solution containing 5 mg. Ir, add 1 drop of NaOH solution. Note the change in color. Boil the solution and shake the tube for a minute. Observe the formation of an azure-blue precipitate.

**5. Action of  $\text{NH}_4\text{Cl}$ .** In a test-tube treat 1 cc. of iridium solution containing 10 mg. Ir with 1 g. of solid  $\text{NH}_4\text{Cl}$ . Shake the mixture till all is dissolved. Continue the addition of solid  $\text{NH}_4\text{Cl}$  1 g. at a time with shaking until an excess of 1 g. is present. Shake the mixture thoroughly. The blackish-red compound which forms is  $(\text{NH}_4)_2\text{IrCl}_6$ .

**6. Action of KCl.** Repeat Exp. 5 using solid KCl instead of  $\text{NH}_4\text{Cl}$ . The brownish-black precipitate is  $\text{K}_2\text{IrCl}_6$ .

**7. Action of Reducing Agents.** Use an iridium solution of strength 1 mg. Ir per cubic centimeter for these tests.

(a) **Oxalic Acid.** To 1 cc. of iridium solution add 1 cc. of oxalic acid solution. Boil. The bleaching is due to the reduction of  $\text{Ir}^{\text{IV}}$  to  $\text{Ir}^{\text{III}}$ .

(b)  **$\text{FeSO}_4$ .** Treat 1 cc. of iridium solution with 3 drops of conc.  $\text{H}_2\text{SO}_4$  and 0.5 g.  $\text{FeSO}_4$ . Boil. Note that the solution is bleached.

(c)  **$\text{SnCl}_2$ .** In a test-tube add to 1 cc. of iridium solution, 1 cc. of  $\text{SnCl}_2$ . Note that the color of the solution is bleached.

(d)  **$\text{Zn} + \text{HCl}$ .** In a small evaporating dish treat 2 cc. of iridium solution with 2 cc. dil. HCl. Add a piece of zinc and note the reduction to metallic Ir.

**Note.** Sodium formate in the presence of a little acetic acid slowly reduces a solution of  $\text{IrCl}_4$ .

**8. Glow Test.** Apply the glow test to 0.5 cc. of iridium solution. For procedure see Exp. 11 under Pt.

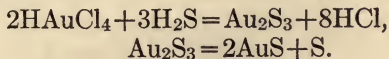
## GOLD

Except where otherwise specified, use a solution of  $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$  of strength 2 mg. Au per cubic centimeter.

**1. (a) Precipitation of  $\text{AuS}$ .** Introduce into a small beaker 5 cc. of gold solution. Add 2.5 cc. dil. HCl. and dilute the solution



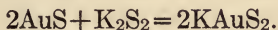
to a volume of 25 cc. Pass in  $\text{H}_2\text{S}$  for several minutes. The black precipitate is  $\text{AuS}$  or  $\text{Au}_2\text{S}_3$ .



Allow the precipitate to settle and pour off the clear solution. Add 10 cc. of water, stir, allow to settle and pour off the water.

(b) **The Insolubility of  $\text{AuS}$  in  $\text{HNO}_3$  and its Solubility in Aqua Regia.** Transfer a small portion of the precipitate to a beaker and demonstrate its insolubility in hot  $\text{HNO}_3$ . Now add  $\text{HCl}$  and heat. Note that the precipitate dissolves.

(c) **Solubility of  $\text{AuS}$  in  $\text{K}_2\text{S}_2$ .** To the remainder of the precipitate of  $\text{AuS}$  in the beaker, add 2 cc. of  $\text{K}_2\text{S}_2$  solution and warm gently. The solution which results contains the gold as a thio salt.



Acidify this solution with dil.  $\text{HCl}$ . The yellowish-brown precipitate which forms is a sulphide, probably  $\text{Au}_2\text{S}_3$ . A control run at the same time with 2 cc. of  $\text{K}_2\text{S}_2$  will make the last result more evident.

**Note.**  $\text{AuS}$  is difficultly soluble in  $(\text{NH}_4)_2\text{S}_x$  hence  $\text{K}_2\text{S}_2$  was used in the above experiment. From a *hot* solution of gold,  $\text{H}_2\text{S}$  gives a brown precipitate of finely divided gold which is soluble in hot  $\text{K}_2\text{S}_2$  with the formation of a thio salt.

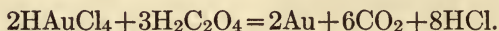
**2. Action of  $(\text{NH}_4)_2\text{S}$ .** Prepare some colorless  $(\text{NH}_4)_2\text{S}$  by passing  $\text{H}_2\text{S}$  for thirty seconds into 5 cc. of dil.  $\text{NH}_4\text{OH}$ . To 1 cc. of gold solution add 5 drops of  $(\text{NH}_4)_2\text{S}$  solution and shake for a few moments. The brownish-black precipitate is  $\text{AuS}$ . Now add 2 cc. of  $(\text{NH}_4)_2\text{S}$  in excess, shake the mixture and heat nearly to boiling. Note that the precipitate practically all dissolves. The minute residue, consisting of exceedingly fine black particles is probably metallic gold.

**3. Action of  $\text{NaOH}$  or  $\text{KOH}$ .** In a test-tube treat 1 cc. of gold solution with 1 drop of  $\text{NaOH}$  and observe that no precipitate forms. **Note.** In more concentrated solutions, however, a reddish-brown precipitate of  $\text{Au}(\text{OH})_3$  is formed. The precipitate resembles  $\text{Fe}(\text{OH})_3$  in appearance, but differs from the latter in the ease with which it dissolves in an excess of the reagent forming sodium aurate  $\text{NaAuO}_2$ .

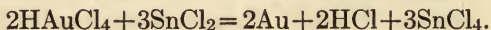
**4. Action of  $\text{NH}_4\text{OH}$ .** To 1 cc. of gold solution add a little dil.  $\text{NH}_4\text{OH}$ . The yellow precipitate is a mixture of gold imino chloride  $\text{Au}(\text{NH})\text{Cl}$  and gold imino amide  $\text{Au}(\text{NH})\text{NH}_2$ . This mixture is also known as fulminating gold because of its property when dried of exploding by warming or by concussion.

The following tests are intended for the detection of small amounts of gold. In making these tests use a solution of gold of strength 0.1 mg. Au per cubic centimeter.

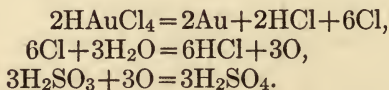
**5. Action of Oxalic Acid.** To 3 cc. of gold solution (see note above) add a few drops of oxalic acid solution and heat to boiling. The precipitate consists of finely divided gold (distinction from Pt).



**6. Action of  $\text{SnCl}_2$ .** (a) In a test-tube treat 3 cc. of gold solution with 1 cc. of conc.  $\text{HCl}$ . From a pipette add 1 drop of  $\text{SnCl}_2$  solution. Shake the mixture and note the colloidal precipitate of gold which slowly forms. The precipitate is called Purple of Cassius. (b) Repeat experiment (a) using 1 cc. of water in place of the conc.  $\text{HCl}$  and observe that a brown solution is obtained.



**7. Action of Sulphurous Acid.** To 3 cc. of gold solution add 1 drop of a saturated aqueous solution of  $\text{SO}_2$ . Note the pink color of the resulting solution. Warm, if necessary to bring out the color.



**8. Action of  $\text{FeSO}_4$ .** In a test-tube treat 3 cc. of gold solution with a few crystals of  $\text{FeSO}_4$ . Observe that the gold is precipitated in the form of a finely divided brown powder.

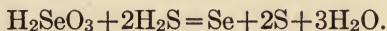
**9. Action of  $\text{H}_2\text{O}_2$  in  $\text{NaOH}$  Solution.** To 3 cc. of gold solution add 5 drops of  $\text{NaOH}$  and 2 cc. of 3 per cent  $\text{H}_2\text{O}_2$ . Shake for a minute and note the formation of colloidal gold.

## SELENIUM

## Reactions of Selenious Compounds

Use a solution of  $\text{H}_2\text{SeO}_3$  of strength 10 mg. Se per cubic centimeter.

1. **Action of  $\text{H}_2\text{S}$ .** Introduce into a small beaker 5 cc. of  $\text{H}_2\text{SeO}_3$  solution. Add 2.5 cc. dil.  $\text{HCl}$  and dilute the solution with water to 25 cc. Pass in  $\text{H}_2\text{S}$ . The lemon-colored precipitate which forms is a mixture of Se and S. Heat to boiling and again pass in  $\text{H}_2\text{S}$ . Observe that the precipitate becomes reddish.



Filter off the precipitate and wash it twice with hot water. Heat 3 cc. of  $(\text{NH}_4)_2\text{S}_x$  and pour the solution on the filter. Catch the liquid which passes through in a test-tube, heat and again pass it through the precipitate. Note that the precipitate dissolves. Acidify the  $(\text{NH}_4)_2\text{S}_x$  solution with dil.  $\text{HCl}$  and observe that the lemon-yellow mixture reprecipitates.

2. **Action of  $(\text{NH}_4)_2\text{S}$ .** To 1 cc. of  $\text{H}_2\text{SeO}_3$  solution add 5 cc. of dil.  $\text{NH}_4\text{OH}$  and pass in  $\text{H}_2\text{S}$ . Note the formation of a reddish-brown solution. Now acidify the solution with dil.  $\text{HCl}$  and note the precipitation of red Se.

3. **Action of  $\text{BaCl}_2$  in Neutral Solution.** In a test-tube treat 1 cc. of  $\text{BaCl}_2$  solution with 3 drops of dil.  $\text{NH}_4\text{OH}$ . Now add 1 cc. of  $\text{H}_2\text{SeO}_3$  solution. The precipitate is  $\text{BaSeO}_3$ . Add 1 cc. of dil.  $\text{HCl}$  and note that the precipitate dissolves.

4. **Action of  $\text{H}_2\text{SO}_3$ .** To 1 cc. of  $\text{H}_2\text{SeO}_3$  solution add 3 cc. of conc.  $\text{HCl}$ . Add 0.2 g. anhydrous  $\text{Na}_2\text{SO}_3$ . The red precipitate is Se.

5. **Action of  $\text{SnCl}_2$ .** Treat 1 cc. of  $\text{H}_2\text{SeO}_3$  solution contained in a test-tube with 1 cc.  $\text{SnCl}_2$  solution. The red precipitate is Se.

6. **Action of  $\text{FeSO}_4$ .** Into a 10 cc. graduate introduce 1 cc. of  $\text{H}_2\text{SeO}_3$  solution and 2 cc. dil.  $\text{HCl}$ . Mix and pour the mixture into a clean test-tube. Clean the graduate and mix in it 1 cc. of  $\text{H}_2\text{SeO}_3$  solution and 2 cc. of conc.  $\text{HCl}$  and transfer the mixed solution to another test-tube. To each test-tube add 0.5 g.  $\text{FeSO}_4$ . Observe that a red precipitate of Se immediately forms in the tube



containing the concentrated acid while none forms in the other tube. Heat the tube in which no precipitate forms to boiling and note the slowly forming precipitate.

**Note.** The action of  $\text{FeSO}_4$  or  $\text{H}_2\text{SO}_3$  in precipitating Se from selenious compounds in strong  $\text{HCl}$  solution, may be utilized to separate Se from Te when present together in solution.

**7. Action of  $\text{Zn} + \text{HCl}$ .** To 1 cc. of  $\text{H}_2\text{SeO}_3$  solution add 1 cc. of dil.  $\text{HCl}$  and a little  $\text{Zn}$ . Note the deposition of Se on the  $\text{Zn}$ .

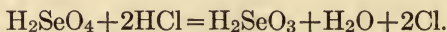
**8. Action of Heat on Se.** Dip the moistened end of a glass rod into some selenium and heat in flame. Note the bluish flame and disagreeable odor.

### Reactions of Selenic Compounds

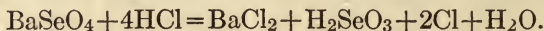
Use a solution of  $\text{K}_2\text{SeO}_4$  of strength 10 mg. Se per cubic centimeter.

**1. Action of  $\text{H}_2\text{S}$ .** (a) Introduce into a small beaker 5 cc. of  $\text{K}_2\text{SeO}_4$  solution. Add 2.5 cc. dil.  $\text{HCl}$  and dilute the solution with water to 25 cc. Pass in  $\text{H}_2\text{S}$ . Observe that no precipitate forms (distinction from selenious compounds). Heat to boiling and again pass in  $\text{H}_2\text{S}$ . Note that even on heating no precipitate forms.

(b) Mix in a small evaporating dish 5 cc. of  $\text{K}_2\text{SeO}_4$  solution and 5 cc. of conc.  $\text{HCl}$ . Heat to boiling and evaporate the solution to 5 cc. Transfer the solution to a small beaker. Dilute with water to 50 cc. and treat with  $\text{H}_2\text{S}$ . A lemon-yellow precipitate of Se will now be obtained. **Note.** The conc.  $\text{HCl}$  reduced the  $\text{H}_2\text{SeO}_4$  to  $\text{H}_2\text{SeO}_3$  from which Se was readily precipitated by  $\text{H}_2\text{S}$ .



**2. Action of  $\text{BaCl}_2$ .** To 1 cc. of  $\text{K}_2\text{SeO}_4$  solution add 1 cc. of dil.  $\text{HCl}$  and 5 drops of  $\text{BaCl}_2$  solution. Shake the mixture. The white precipitate is  $\text{BaSeO}_4$  (distinction from selenious acid). Add 2 cc. of conc.  $\text{HCl}$  and boil. Note that the precipitate dissolves with the evolution of chlorine (distinction from  $\text{BaSO}_4$ ).



**3. Action of  $\text{H}_2\text{SO}_3$ .** (a) In a test-tube treat 1 cc. of  $\text{K}_2\text{SeO}_4$  solution with 1 cc. of conc.  $\text{HCl}$  and 0.2 g.  $\text{Na}_2\text{SO}_3$ . Observe that



no reduction takes place. Now heat the mixture and note the formation of a red precipitate of Se.

(b) In a small evaporating dish or test-tube, boil down a mixture of 1 cc. of  $K_2SeO_4$  solution and 1 cc. of conc. HCl to 1 cc. Cool. Add 1 cc. of conc. HCl and 0.2 g.  $Na_2SO_3$ . Account for the difference in the results obtained in (a) and (b).

## TELLURIUM

### Reactions of Tellurous Compounds

Use a solution of  $K_2TeO_3$  of strength 10 mg. Te per cubic centimeter.

1. **Action of Dil. HCl on  $K_2TeO_3$ .** To 1 cc. of  $K_2TeO_3$  solution add 1 drop of dil. HCl. The precipitate is  $H_2TeO_3$ . Now add several more drops of dil. HCl and note that the precipitate dissolves.

2. **Action of  $H_2S$ .** Introduce into a small beaker 5 cc. of  $K_2TeO_3$  solution. Add 2.5 cc. dil. HCl and dilute the solution with water to 25 cc. Pass in  $H_2S$ . The brown precipitate is  $TeS_2$ . Filter it off and wash it several times with water. Pass twice through the filter 2 cc. of warm  $(NH_4)_2S_x$  and catch the solution in a test-tube. Observe that  $TeS_2$  is soluble in  $(NH_4)_2S_x$ . Acidify the  $(NH_4)_2S_x$  solution with dil. HCl. The brown precipitate is  $TeS_2$ .

3. **Action of  $H_2SO_3$ .** In a 10 cc. graduate mix 1 cc. of  $K_2TeO_3$  solution with 3 cc. of conc. HCl and pour the solution into a test-tube. Into a second test-tube introduce a solution prepared by mixing 1 cc. of  $K_2TeO_3$  solution with 3 cc. of dilute HCl. To each tube add 0.2 g. anhydrous  $Na_2SO_3$ . Shake and heat each to boiling. Note that a black precipitate of Te forms only in the tube containing the dil. HCl. What conclusion can you draw from these experiments as to the influence of the concentration of the HCl on the precipitation of Te by  $H_2SO_3$ ? Does a high concentration of HCl interfere with the precipitation of Se (ous) by  $H_2SeO_3$  (see Exp. 4 under Se (ous))? How would you separate Se from Te in a solution containing both? **Note.** A white precipitate of NaCl separates in the tube containing the conc. HCl. If after boiling, the solution be diluted with water, a precipitate of Te will be obtained.

4. **Action of Zn+HCl.** To 1 cc. of  $K_2TeO_3$  solution add 1 cc. of dil. HCl and a small piece of granulated Zn. Note the black deposit of Te on the Zn.

5. **Action of  $SnCl_2$ .** In a test-tube treat 1 cc. of  $K_2TeO_3$  solution with 1 cc. of  $SnCl_2$ . Note the black precipitate of Te.

6. **Action of  $FeSO_4$ .** Treat 1 cc. of  $K_2TeO_3$  solution with 2 cc. of dil. HCl and 0.5 g.  $FeSO_4$ . Heat to boiling and note that Te does not precipitate (distinction from Se).

7. **Action of Magnesia Mixture.** To 1 cc. of  $K_2TeO_3$  solution add 1 cc. of magnesia mixture. Note the formation of a white precipitate (distinction from Se).

### Reactions of Telluric Compounds

Use a solution of  $H_2TeO_4 \cdot 2H_2O$  of strength 10 mg. Te per cubic centimeter.

1. **Action of  $H_2S$ .** (a) Introduce into a small beaker 5 cc. of  $H_2TeO_4$  solution. Add 2.5 cc. dil. HCl and dilute the solution with water to 25 cc. Do not heat the solution. Pass in  $H_2S$ . Observe that no precipitate forms (distinction from  $H_2TeO_3$ ). Now heat the solution to boiling and pass in  $H_2S$ . Note the slight precipitate which is obtained.

(b) In a small evaporating dish mix 5 cc. of  $H_2TeO_4$  solution with 5 cc. of conc. HCl. Heat to boiling and evaporate the solution to 5 cc. Cool. Dilute the solution with water to 50 cc. and treat with  $H_2S$ . The brown precipitate which immediately forms is  $TeS_2$ . Explain the results in (a) and (b).

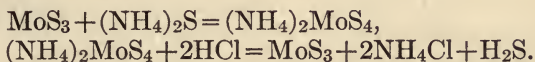
2. **Action of  $SnCl_2$ .** In a test-tube treat 1 cc. of  $H_2TeO_4$  with 1 cc. of  $SnCl_2$ . Observe that no reduction takes place. Heat the mixture to boiling and shake. The black precipitate is Te.

### MOLYBDENUM

**Solution A.** A stock solution of ammonium molybdate of strength 100 mg. Mo per cubic centimeter may be prepared as follows: In a beaker dilute 14.2 cc. conc.  $NH_4OH$  with water to a volume of 50 cc. To the resulting solution add with stirring, 15 g.  $MoO_3$  (99–100 per cent) and stir until nearly all the  $MoO_3$  is dissolved. Dilute with water to 100 cc., stir, and heat to boiling. Filter if the solution is not perfectly clear.

**Solution B.** Dilute 10 cc. of Solution A with water to 100 cc. Mix thoroughly. This solution will have a concentration of 10 mg. Mo per cubic centimeter.

1. **Action of  $\text{H}_2\text{S}$ .** Introduce into a small beaker 1 cc. of molybdate solution A. Add 2.5 cc. dil. HCl and dilute the solution with water to 25 cc.; **very slowly** with stirring run in  $\text{H}_2\text{S}$  one bubble at a time until 5–10 have been introduced. Note the blue color of the solution. Now pass in more  $\text{H}_2\text{S}$  until precipitation is complete. The brownish-black precipitate is  $\text{MoS}_3$ . Heat the mixture to coagulate the precipitate; filter, and wash it twice with small amounts of hot water. Pour on the filter 2 cc. of warm  $(\text{NH}_4)_2\text{S}_x$  and catch the filtrate in a test-tube. Note that some of the  $\text{MoS}_3$  dissolves in the  $(\text{NH}_4)_2\text{S}_x$  yielding a solution of reddish color. Acidify this solution with dil. HCl. The precipitate is  $\text{MoS}_3$ .



2. **Action of Dilute Mineral Acids on Strong Solutions of Alkali Molybdates.** To 1 cc. of molybdate solution A add dil. HCl drop by drop. The white precipitate is  $\text{H}_2\text{MoO}_4$ . Now add more dil. HCl and observe that the precipitate is soluble in an excess of the reagent.

3. **Action of  $(\text{NH}_4)_2\text{S}$ .** In a test-tube treat 1 cc. of molybdate solution B with 1 cc. of  $(\text{NH}_4)_2\text{S}$ . Observe first, that no precipitate forms; explain. Second, that the solution on standing for five minutes takes on an orange-red color. Acidify the solution with dil. HCl. What is the brown precipitate which separates? For equations see Exp. 1 above.

4. **Action of Alkali Phosphate.** To 3 cc. of molybdate solution B add 2 cc. of dil.  $\text{HNO}_3$ . Add 1 drop of  $\text{Na}_2\text{HPO}_4$  solution, mix thoroughly, heat, and allow to stand. What is the precipitate which forms? Write its formula.

5. **Action of Reducing Agents.** (a)  **$\text{SnCl}_2$ .** Introduce into a 10 cc. graduate 1 cc. of molybdate solution B, 1 cc. of dil. HCl and 8 cc. of water. Transfer the mixed solution to a test-tube and add from a pipette 1 drop of  $\text{SnCl}_2$  solution. Mix thoroughly and note the blue color.

(b) **Zn.** To 1 cc. of molybdate solution B add 1 cc. of dil. HCl



and a small piece of Zn. Note the successive changes in color from blue to green and finally to brown.

(c) **KCNS in the Presence of a Reducing Agent Such as  $\text{Zn} + \text{HCl}$  or  $\text{SnCl}_2$ .** In a test-tube treat 1 cc. of molybdate solution B with 1 cc. of dil. HCl and 1 cc. of KCNS solution. Observe that the solution turns yellow. Now add a small piece of Zn. The solution becomes carmine-red because of the formation of molybdenum thiocyanate. The same red compound is formed when a drop of  $\text{SnCl}_2$  is added instead of Zn.

**Note.** The deep red coloration is not destroyed by the addition of phosphoric acid (distinction from  $\text{Fe}(\text{CNS})_3$ ). It is, however, prevented from forming by the presence of tartaric acid and other organic acids.

**6. Formation of Permolybdate.** To 1 cc. of molybdate solution B add 1 cc. of dil.  $\text{NH}_4\text{OH}$  and 2 cc. of 3 per cent  $\text{H}_2\text{O}_2$ . The red color is due to the formation of ammonium permolybdate.

**7. Action of  $\text{K}_4\text{Fe}(\text{CN})_6$ .** In a test-tube treat 1 cc. of molybdate solution B with 1 cc. of dil. HCl and a little  $\text{K}_4\text{Fe}(\text{CN})_6$ . The reddish-brown precipitate is molybdenum ferrocyanide. Show that it is soluble in  $\text{NH}_4\text{OH}$ ; also in NaOH (distinction from uranyl and cupric ferrocyanide).

### GROUP 3

**Division A.** Beryllium, titanium, thorium, zirconium, columbium, tantalum, uranium, cerium, lanthanum, praseodymium, neodymium, yttrium, erbium.

**Division B.** Vanadium.

### BERYLLIUM

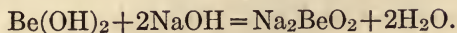
Use a solution of  $\text{BeSO}_4$  of strength 2 mg. Be per cubic centimeter.

**1. Action of  $\text{NH}_4\text{OH}$ .** To 2 cc.  $\text{BeSO}_4$  solution add 2 drops of dil.  $\text{NH}_4\text{OH}$  and then 2 cc. in excess. The white precipitate is  $\text{Be}(\text{OH})_2$  resembling in appearance  $\text{Al}(\text{OH})_3$ . Note that it is insoluble in an excess of the precipitant. Now add an excess (3 cc.) of dil. HCl and observe that the precipitate dissolves.

**2. Action of NaOH. Note.** If the NaOH solution is not perfectly clear, filter it through cotton before making the following



experiment. Treat 2 cc. of  $\text{BeSO}_4$  in a test-tube with 2 drops of clear  $\text{NaOH}$  solution and then add 1 cc. in excess. Observe that the precipitate which first forms redissolves.



Transfer the solution to a small beaker, dilute with 20 cc. of water, boil for one-half minute and allow the beaker to stand for a minute. Observe that  $\text{Be}(\text{OH})_2$  has been reprecipitated.

**3. Action of  $(\text{NH}_4)_2\text{S}$ .** To 2 cc. of  $\text{BeSO}_4$  solution add 1 cc. of dil.  $\text{NH}_4\text{OH}$  and then pass in  $\text{H}_2\text{S}$ . Note that the precipitate remains unchanged and that it is insoluble in an excess of the reagent.

**4. Action of  $\text{Na}_2\text{CO}_3$ .** In a test-tube treat 2 cc. of  $\text{BeSO}_4$  solution with one drop of  $\text{Na}_2\text{CO}_3$  solution. Now add 2 cc. in excess and filter. Boil the filtrate. The precipitate which forms is a basic beryllium carbonate.

**5. Action of  $(\text{NH}_4)_2\text{CO}_3$ .** To 2 cc. of  $\text{BeSO}_4$  solution, add 2 drops of a saturated solution of  $(\text{NH}_4)_2\text{CO}_3$ . The precipitate is basic beryllium carbonate. Now add 5 cc. in excess, shake vigorously and allow the tube to stand for a minute. Note that the precipitate completely dissolves. Pour the solution into a small beaker and boil for one minute. Note the reprecipitation of basic beryllium carbonate (method of separation from Al and Fe).

**6. Action of  $\text{NaHCO}_3$ .** To 5 cc. of  $\text{BeSO}_4$  solution add 0.2 g. solid  $\text{NaHCO}_3$  and shake the mixture vigorously. Note the formation of a precipitate. Now add 0.5 g. of  $\text{NaHCO}_3$ , heat the mixture to boiling, boil for a few minutes and allow it to stand. Observe that the precipitate completely dissolves (method of separating Be from Al, Fe and Ti).

**7. Action of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  or  $\text{H}_2\text{C}_2\text{O}_4$ .** (a) Treat 2 cc. of  $\text{BeSO}_4$  solution with 1 cc.  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution and boil. Note that no precipitate forms (distinction from Th, Zr, Ce, Er, Y, La, Pr and Nd). (b) Repeat Exp. (a) using 1 cc. of oxalic acid instead of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . Note that the result is the same as in (a).

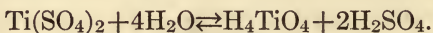
**8. Action of  $\text{K}_2\text{SO}_4$ .** To 2 cc. of  $\text{BeSO}_4$  solution add 2 cc. of a saturated aqueous solution of  $\text{K}_2\text{SO}_4$ . Shake vigorously and then boil the solution. Observe that no precipitate forms (distinction from Zr, Th, Ce, La, Pr, and Nd).

## TITANIUM

Use a solution of  $\text{Ti}(\text{SO}_4)_2$  of strength 10 mg. Ti per cubic centimeter prepared as follows: Introduce into a small beaker 10 cc. of conc.  $\text{H}_2\text{SO}_4$ . Add with stirring 1 g. of  $\text{TiO}_2 \cdot \text{H}_2\text{O}$  and heat with constant stirring till complete solution takes place. Pour contents of beaker **cautiously**, a little at a time, into 40 cc. of water. Mix thoroughly and cool.

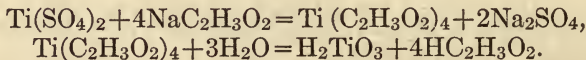
1. **Action of  $\text{NH}_4\text{OH}$ .** To 2 cc. of  $\text{Ti}(\text{SO}_4)_2$  solution add  $\text{NH}_4\text{OH}$  to alkaline reaction. The white precipitate is  $\text{Ti}(\text{OH})_4$ . Add an excess of the reagent and note that the precipitate is practically insoluble in excess. Transfer a portion of the suspended precipitate to another test-tube and add an excess of conc.  $\text{HCl}$ . Observe that the precipitate dissolves. **Note.** With  $\text{NaOH}$ ,  $\text{KOH}$  or  $(\text{NH}_4)_2\text{S}$  the same compound is precipitated. If the solution is hot, these reagents precipitate metatitanic acid  $\text{H}_2\text{TiO}_3$  which is difficultly soluble in acids.

2. **Action of Water.** (a) In a beaker dilute 2 cc. of  $\text{Ti}(\text{SO}_4)_2$  solution with 50 cc. of water and heat to boiling. Note cloudiness due to precipitation of  $\text{H}_4\text{TiO}_4$ .

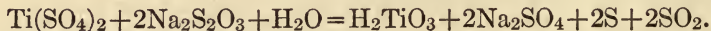


(b) In a beaker treat 2 cc. of  $\text{Ti}(\text{SO}_4)_2$  solution with 1 cc. of conc.  $\text{H}_2\text{SO}_4$  and 49 cc. of water; mix and heat the solution to boiling. Explain why the solution remains clear. Keep this solution for the next experiment.

(c) To the boiling solution of Exp. 2b above, add 5 g.  $\text{NaC}_2\text{H}_3\text{O}_2$ . Note and account for the precipitate which forms.



3. **Action of  $\text{Na}_2\text{S}_2\text{O}_3$ .** In a test-tube treat 1 cc. of  $\text{Ti}(\text{SO}_4)_2$  solution with 0.2 g.  $\text{Na}_2\text{S}_2\text{O}_3$  and boil the mixture. The precipitate consists of  $\text{H}_2\text{TiO}_3 + \text{S}$ .



4. **Action of  $\text{H}_2\text{O}_2$ .** (a) To 1 cc. of  $\text{Ti}(\text{SO}_4)_2$  solution add 1 cc. of 3 per cent  $\text{H}_2\text{O}_2$ . The orange-red color is due to the formation of  $\text{TiO}_2 \cdot \text{H}_2\text{O}_2$ .

(b) **Action of  $\text{H}_2\text{O}_2$  in More Dilute Solutions.** Dilute 1 cc. of  $\text{Ti}(\text{SO}_4)_2$  solution with water to 100 cc. Mix thoroughly and to 1 cc. of this solution in a test-tube add 1 cc. of 3 per cent  $\text{H}_2\text{O}_2$ . Observe the yellow coloration. **Note.** Reserve some of the dilute solution of  $\text{Ti}(\text{SO}_4)_2$  for Exp. 6b.

**Note.** This test for Ti is capable of detecting in  $\text{H}_2\text{SO}_4$  solution 0.005 per cent  $\text{TiO}_2$  with certainty; but it is only reliable in the absence of cerium, molybdate, vanadate and chromate ions.

5. **Action of Reducing Agents. Zn or Sn.** To 2 cc. of  $\text{Ti}(\text{SO}_4)_2$  solution add a piece of zinc and warm the mixture gently. The violet color which develops is due to the formation of  $\text{Ti}_2(\text{SO}_4)_3$ . **Note.** Neither  $\text{H}_2\text{S}$  nor  $\text{H}_2\text{SO}_3$  reduces tetravalent Ti (distinction from ferric ion).

6. **Action of Cupferron.** (The  $\text{NH}_4$  salt of phenyl-nitrosohydroxylamine  $\text{C}_6\text{H}_5\text{NO} \cdot \text{NONH}_4$ ) (a) To 2 cc. of  $\text{Ti}(\text{SO}_4)_2$  solution add 1 cc. of a 6 per cent aqueous solution of cupferron. The yellow precipitate is  $\text{Ti}(\text{C}_6\text{H}_5\text{NONO})_4$ . (b) To 5 cc. of the dilute Ti solution reserved in Exp. 4b add 1 cc. of cupferron solution. Observe the formation of a yellow precipitate.

**Note.** Ferric ions give a red precipitate with this reagent. To test for Ti in solutions containing Fe, proceed as follows: To the acid solution add  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$  in amount equal to about four times the weight of Ti and Fe present. Treat with  $\text{H}_2\text{S}$  till all the Fe is reduced. Then precipitate the Fe as  $\text{FeS}$  by making the solution alkaline with  $\text{NH}_4\text{OH}$  and treating again with  $\text{H}_2\text{S}$ . Filter off the  $\text{FeS}$ , acidify the filtrate with  $\text{H}_2\text{SO}_4$ , boil to expel the  $\text{H}_2\text{S}$  and finally precipitate the Ti with cupferron.

7. **Action of  $\text{K}_4\text{Fe}(\text{CN})_6$ .** To 2 cc. of  $\text{Ti}(\text{SO}_4)_2$  solution add 1 cc. of  $\text{K}_4\text{Fe}(\text{CN})_6$  solution. Shake the tube for a minute and observe the formation of a brown precipitate.

8. **Action of  $\text{Na}_2\text{HPO}_4$ .** In a test-tube treat 2 cc. of  $\text{Ti}(\text{SO}_4)_2$  solution with 1 cc. of  $\text{Na}_2\text{HPO}_4$  solution and shake the mixture for a minute. The white precipitate is basic titanate phosphate  $\text{TiOHPO}_4$ .



## THORIUM

Use a solution of  $\text{Th}(\text{NO}_3)_4$  of strength 10 mg. Th per cubic centimeter.

1. **Action of  $\text{NH}_4\text{OH}$ .** To 2 cc. of thorium solution add 2 drops of dil.  $\text{NH}_4\text{OH}$  and then add 2 cc. in excess. The white precipitate is  $\text{Th}(\text{OH})_4$ . Note that it is insoluble in excess of the reagent. Now add an excess (3 cc.) of dilute  $\text{HCl}$  and observe that the precipitate dissolves.

2. **Action of  $\text{NaOH}$ .** Repeat Exp. 1 using  $\text{NaOH}$  instead of  $\text{NH}_4\text{OH}$ . Note that  $\text{Th}(\text{OH})_4$  is insoluble in excess of  $\text{NaOH}$ .

3. **Action of  $(\text{NH}_4)_2\text{S}$ .** In a test-tube treat 2 cc. of thorium solution with 1 cc. of dil.  $\text{NH}_4\text{OH}$ . Treat the mixture with  $\text{H}_2\text{S}$ . Note that the  $\text{Th}(\text{OH})_4$  remains unchanged and is insoluble in an excess of the precipitant.

4. **Action of  $\text{Na}_2\text{CO}_3$ .** To 2 cc. of  $\text{Th}(\text{NO}_3)_4$  solution add 2 drops of  $\text{Na}_2\text{CO}_3$  solution and then 2 cc. in excess. Note that the carbonate which first forms is soluble in an excess of the reagent. Heat the solution to boiling and observe that reprecipitation takes place. To the precipitate in the tube add an excess of dil.  $\text{HCl}$  and observe that the precipitate completely dissolves.

5. **Action of  $\text{K}_2\text{SO}_4$ .** To 2 cc. of  $\text{Th}(\text{NO}_3)_4$  solution add 2 cc. of a saturated aqueous solution of  $\text{K}_2\text{SO}_4$ . Shake the tube vigorously for a minute and allow it to stand for two minutes. The crystalline precipitate which forms is a double sulphate of Th and K having the formula  $\text{Th}(\text{SO}_4)_2 \cdot 2\text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$  (distinction from Al, Be, and Yttria earths). Add 2 cc. of  $\text{K}_2\text{SO}_4$  in excess and observe that the precipitate does not dissolve. **Note.** The corresponding Na salt is soluble in water as well as in a saturated solution of  $\text{Na}_2\text{SO}_4$ .

6. **Action of Oxalic Acid.** Treat 2 cc. of  $\text{Th}(\text{NO}_3)_4$  solution with 1 cc. of  $\text{H}_2\text{C}_2\text{O}_4$  solution. The white crystalline precipitate is  $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ . Divide the precipitate into 2 equal portions. To one add 2 cc. more of the reagent. To the other add 5 cc. dil.  $\text{HCl}$ . Observe that the precipitate is practically insoluble in an excess of either reagent.

7. **Action of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ .** (a) To 2 cc. of  $\text{Th}(\text{NO}_3)_4$  solution add 1 cc. of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution. The precipitate is  $\text{Th}(\text{C}_2\text{O}_4)_2$  (distinction from Al and Be). Add 3 cc. of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  in excess



and boil the mixture. The solubility of the precipitate in an excess of the reagent is due to the formation of a double oxalate of  $\text{NH}_4$  and Th. To the clear solution add 1 cc. of dil. HCl. Note that  $\text{Th}(\text{C}_2\text{O}_4)_4$  is reprecipitated (distinction from Zr). (b) Prepare some  $\text{Th}(\text{C}_2\text{O}_4)_2$  as directed in (a). Add 5 cc. of  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  solution and boil the mixture. Note that the precipitate dissolves. Now add 3 cc. dil. HCl and note the reprecipitation of  $\text{Th}(\text{C}_2\text{O}_4)_2$ . (c) Prepare some  $\text{Th}(\text{C}_2\text{O}_4)_2$  as directed in (a). Add 5 cc. dil. HCl and shake the mixture. Note that the precipitate is not readily soluble.

8. **Action of  $\text{Na}_2\text{HPO}_4$ .** In a test-tube treat 2 cc. of  $\text{Th}(\text{NO}_3)_4$  solution with 0.5 cc.  $\text{Na}_2\text{HPO}_4$  solution. The precipitate is  $\text{Th}_3(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$ .

9. **Action of KF.** To 2 cc. of thorium solution add 1 cc. of KF solution. Note the gelatinous precipitate that forms. Set the tube aside for one-half hour and observe that the precipitate becomes granular.

10. **Action of  $\text{K}_4\text{Fe}(\text{CN})_6$ .** Treat 2 cc. of thorium solution with a little  $\text{K}_4\text{Fe}(\text{CN})_6$ . Note the formation of a white precipitate.

11. **Action of  $\text{Na}_2\text{S}_2\text{O}_3$ .** In a test-tube treat 2 cc. of  $\text{Th}(\text{NO}_3)_4$  solution with 0.2 g.  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  and boil the solution. The precipitate is a mixture of  $\text{Th}(\text{OH})_4$  and a basic thiosulphate admixed with sulphur (distinction from Ce and Yttria earths except Se).

12. **Action of  $\text{H}_2\text{O}_2$ .** To 2 cc. of  $\text{Th}(\text{NO}_3)_4$  solution add 1 cc. of 3 per cent  $\text{H}_2\text{O}_2$  and heat. Note the white gelatinous precipitate which forms (distinction from Zr).

13. **Action of Metanitrobenzoic Acid.** In a test-tube treat 2 cc. of  $\text{Th}(\text{NO}_3)_4$  solution with 2 cc. of a 0.4 per cent aqueous solution of metanitrobenzoic acid. The white precipitate is thorium metanitrobenzoate (distinction from Ce, La, Pr, and Nd).

## ZIRCONIUM

Use a solution of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  of strength 10 mg. Zr per cubic centimeter.

1. **Action of  $\text{NH}_4\text{OH}$ .** To 2 cc. of zirconium solution add 2 drops of dil.  $\text{NH}_4\text{OH}$  and then 1 cc. in excess. Observe that the

flocculent precipitate of  $\text{Zr}(\text{OH})_4$  is insoluble in an excess of the reagent. Add to the precipitate in the tube an excess (3 cc.) of dil.  $\text{HCl}$  and shake the mixture vigorously. Note that the precipitate dissolves.

**2. Action of  $\text{NaOH}$ .** (a) In a test-tube treat 2 cc. of zirconium solution with 2 drops of  $\text{NaOH}$  solution and then add 1 cc. in excess. Note that the precipitate is insoluble in excess (distinction from  $\text{Be}$  and  $\text{Al}$ ). To the precipitate add 5 cc. dil.  $\text{HCl}$ . Shake the mixture and allow the tube to stand for a few moments. Note that the precipitate completely dissolves.

(b) To 2 cc. of zirconium solution add 1 cc. of  $\text{NaOH}$  solution and boil the suspended precipitate. Now add 5 cc. of dil.  $\text{HCl}$  and shake the mixture. Note that the precipitate does not dissolve readily.

**3. Action of  $(\text{NH}_4)_2\text{S}$ .** Treat 2 cc. of zirconium solution in a test-tube with 1 cc. of dil.  $\text{NH}_4\text{OH}$ . Pass  $\text{H}_2\text{S}$  into the mixture. Observe that the precipitate remains unchanged and that it is insoluble in excess of the reagent. **Note.** The sulphide cannot be formed in the wet way.

**4. Action of  $(\text{NH}_4)_2\text{CO}_3$ .** To 2 cc. of zirconium solution add 1 drop of  $(\text{NH}_4)_2\text{CO}_3$  and shake the mixture. The flocculent precipitate which forms is basic zirconium carbonate ( $3\text{ZrO}_2 \cdot \text{CO}_2 \cdot 8\text{H}_2\text{O}$ ). Now add 5 drops in excess and observe how readily the precipitate dissolves in excess (distinction from  $\text{Al}$ ). Boil the solution for one-half minute. The substance which precipitates is  $\text{Zr}(\text{OH})_4$ .

**5. Action of  $\text{Na}_2\text{CO}_3$ .** (a) Treat 3 cc. of zirconium solution with one drop of  $\text{Na}_2\text{CO}_3$  solution. Note the formation of a precipitate. Now add 3 drops in excess and shake the mixture. Observe that the precipitate dissolves in excess (distinction from  $\text{Al}$ ). Boil the solution. The substance which precipitates is  $\text{Zr}(\text{OH})_4$ .

(b) To 3 cc. of zirconium solution add 1 drop of  $\text{Na}_2\text{CO}_3$  solution and then add 3 drops in excess. Shake the tube till solution takes place. To the clear solution add 2 cc. dil.  $\text{NH}_4\text{OH}$ . The precipitate is  $\text{Zr}(\text{OH})_4$ .

**6. Action of Oxalic Acid.** (a) To 2 cc. of zirconium solution add 1 drop of oxalic acid. The white precipitate is zirconium oxalate. Now add 4 drops in excess and observe that the precipitate is readily soluble in excess.

(b) Prepare some zirconium oxalate by adding 1 drop of oxalic

acid to 2 cc. of zirconium solution. Divide the precipitate into 2 equal portions. To one add 3 cc. of dil. HCl and observe that the precipitate does not readily dissolve. To the other portion add 1 cc.  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution. Note that the precipitate readily dissolves.

**7. Action of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ .** (a) In a test-tube treat 2 cc. of zirconium solution with 2 drops of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution and then add 5 drops in excess. Observe that the precipitate of  $\text{Zr}(\text{C}_2\text{O}_4)_2$  readily dissolves in excess. To the clear solution add 1 cc. of dil.  $\text{NH}_4\text{OH}$ . The precipitate is  $\text{Zr}(\text{OH})_4$ .

(b) To 2 cc. of zirconium solution add 2 drops of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution and then 1 cc. in excess. Observe that the precipitate dissolves readily in excess. To the clear solution add 1 cc. of dil. HCl. Repeatedly filter through a double filter if any precipitate forms (see note below) until a clear filtrate is obtained. To the latter add  $\text{NH}_4\text{OH}$  to alkaline reaction.

**Note.** From an  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution of zirconium oxalate, HCl fails to reprecipitate  $\text{Zr}(\text{C}_2\text{O}_4)_2$  (distinction from Th). The solution was filtered in Exp. 7b because of the presence of some impurity in the zirconium solution. The relatively large precipitate finally obtained with  $\text{NH}_4\text{OH}$  in the filtrate shows that practically all of the Zr remained in solution on adding the HCl.

**8. Action of  $\text{Na}_2\text{HPO}_4$ .** Treat 2 cc. of zirconium solution with 5 cc. of dil.  $\text{H}_2\text{SO}_4$ . Mix well and then add 1 cc. of  $\text{Na}_2\text{HPO}_4$ . The precipitate is a basic phosphate possessing the formula  $\text{Zr}(\text{OH})\text{PO}_4$ . (Distinction from Fe, Ti, and Cr).

**9. Action of  $\text{K}_4\text{Fe}(\text{CN})_6$ .** To 2 cc. of zirconium solution add a few drops of  $\text{K}_4\text{Fe}(\text{CN})_6$  solution. Note the white precipitate of  $\text{ZrFe}(\text{CN})_6$  which forms.

**10. Action of  $\text{H}_2\text{O}_2$ .** (a) Treat 2 cc. of zirconium solution with 1 cc. of 3 per cent  $\text{H}_2\text{O}_2$ . Observe that **no** precipitate forms.

(b) Repeat experiment (a) using 1 cc. of 30 per cent  $\text{H}_2\text{O}_2$ . Note that **no** precipitate forms.

**Note.** Working with more concentrated solutions of Zr, the author was unable to get a precipitate either with the dilute or concentrated peroxide. Heating the mixed solutions or allowing them to stand for hours, also failed to induce precipitation. These observations are at variance with the statement made by Fresenius, Treadwell-Hall, Herzfeld and Korn, and Classen, that zirconium solutions may be precipitated by  $\text{H}_2\text{O}_2$ .



**11. Action of  $K_2SO_4$ .** To 2 cc. of zirconium solution add 3 cc. of a saturated aqueous solution of  $K_2SO_4$ . Shake the tube vigorously for a minute and allow it to stand for five minutes. The white precipitate is a double sulphate of K and Zr. It is insoluble in an excess of the reagent (distinction from Al and Be and Yttria earths). To the precipitate in the test-tube add 5 cc. dil. HCl, shake the mixture vigorously and allow it to stand for a minute or two. Note that the precipitate dissolves.

**12. Action of Turmeric Solution.** In a 10 cc. graduate mix 1 cc. of water, 1 cc. of dil. HCl, 5 cc. of methyl alcohol and 1 cc. of an alcoholic solution of turmeric. Transfer the mixed solution to a test-tube. This is the control or blank. Clean the graduate and in it measure 1 cc. of zirconium solution, 1 cc. dil. HCl, 5 cc. of methyl alcohol and 1 cc. of turmeric solution. Mix well and pour the solution into another clean test-tube. Compare the tubes and observe that the blank is light yellow while the solution in the tube containing the Zr is reddish-brown.

**13. Action of HF.** To 2 cc. of zirconium solution in a platinum crucible, add 2 cc. of 48 per cent HF. Stir the solution with a hard rubber stirring rod and note the absence of precipitation (distinction from Th, Ce and Y, each of which under the same conditions gives a precipitate).

**14. Action of  $Na_2S_2O_3$ .** To 2 cc. of zirconium solution add 0.2 g. of  $Na_2S_2O_3$ , and heat to boiling; the precipitate is  $Zr(OH)_4 + S$ , (Method of separation from Ce and distinction from Y, Pr and Nd).

**15. Action of  $H_2SO_3$ .** In a test-tube treat 2 cc. of zirconium solution with 2 drops of dil. HCl and 2 cc. of a saturated aqueous solution of  $SO_2$ . Heat to boiling. The precipitate is  $Zr(OH)_4$ . (Baskerville's method of separating Zr from Fe and Al.)

## COLUMBIUM OR NIOBIUM

**1. Solubility of  $Cb_2O_5$  in HF and the Preparation of a Solution of Columbium.** Into a platinum crucible introduce 30 mg.  $Cb_2O_5$  (equivalent to 20 mg. Cb). Add 2 cc. of 48 per cent HF and heat gently under hood on a sand bath or asbestos board. Note that the oxide completely dissolves. Cool, add 2 cc. of conc.  $H_2SO_4$  and evaporate till  $SO_3$  fumes are given off copiously. This is to



make sure that all the HF has been removed. (If the solution has a dark color indicating the presence of organic matter, cool the solution, add 1 cc. of conc.  $\text{HNO}_3$  and evaporate again to  $\text{SO}_3$  fumes.) Note that the  $\text{H}_2\text{SO}_4$  solution is perfectly clear. Cool thoroughly. To 5 cc. of cold water in a small beaker add the contents of crucible, a little at a time with stirring. Note that the diluted solution is perfectly clear. This will not be the case if larger amounts of Cb are used or if the solution is allowed to get hot.

**2. Action of  $\text{Zn} + \text{HCl}$ .** Introduce 2 cc. of the columbium solution prepared above into a test-tube. Add 2 cc. dil. HCl and 0.5 g. granular zinc. Note the dirty blue color which develops at the end of about one-half minute (distinction from Ta).

**3. Action of  $\text{NH}_4\text{OH}$ .** To the remainder of the columbium solution add conc.  $\text{NH}_4\text{OH}$  to alkaline reaction. The white precipitate is columbic or niobic acid. Add dil. HCl to acid reaction and then 2 cc. in excess. Note that the precipitate is insoluble in dil. HCl. Reserve this mixture for the following experiment.

**4. Action of  $\text{H}_2\text{O}_2$  on Columbic Acid in the Presence of HCl.** To the mixture of columbic acid and dil. HCl, add 5 cc. 3 per cent  $\text{H}_2\text{O}_2$  and heat to boiling. Note that complete solution takes place. Reserve this solution for the following experiments.

**5. Action of  $\text{NH}_4\text{OH}$  on the  $\text{H}_2\text{O}_2$  Solution of Columbic Acid.**

(a) Render alkaline with  $\text{NH}_4\text{OH}$  1 cc. of the  $\text{H}_2\text{O}_2$  solution obtained in Exp. 4. Note that no precipitation takes place.

(b) To 1 cc. of the  $\text{H}_2\text{O}_2$  solution of columbic acid, add 1 cc. of  $\text{H}_2\text{SO}_3$  and then render the solution alkaline with  $\text{NH}_4\text{OH}$ . Note that precipitation now takes place. **Note.** In the above experiment the  $\text{H}_2\text{SO}_3$  destroyed the  $\text{H}_2\text{O}_2$ . The  $\text{H}_2\text{O}_2$  may also be removed by adding  $\text{H}_2\text{SO}_4$  and evaporating the solution to  $\text{SO}_3$  fumes.

**6. Action of Conc.  $\text{H}_2\text{SO}_4$  on the  $\text{H}_2\text{O}_2$  Solution of Columbic Acid.** Pour into an evaporating dish the remainder of the  $\text{H}_2\text{O}_2$  solution reserved in Exp. 4. Add 2 cc. of conc.  $\text{H}_2\text{SO}_4$  and evaporate the solution to  $\text{SO}_3$  fumes. Cool. Add 5 cc. of cold water and stir till a uniform solution results. Divide the solution into two portions. To the first in a test-tube add 2 cc. dil. HCl and 0.5 g. zinc. Note the blue color which develops at the end of thirty seconds. Make the other portion alkaline with  $\text{NH}_4\text{OH}$  and note the precipitation of columbic acid. Pass  $\text{H}_2\text{S}$  into the

suspension of columbic acid and note that the precipitate remains unchanged.

### TANTALUM

**1. Preparation of Potassium Tantalate Solution.** In a platinum crucible mix 125 mg. of  $Ta_2O_5$  (equivalent to 100 mg. Ta) with 1 g. anhydrous  $K_2CO_3$ . Cover the crucible and heat it with a Meeker burner till no more  $CO_2$  is given off and until the melt is **perfectly** transparent. Cool. Treat the melt in the crucible with 10 cc. of water, and stir until the melt is completely dissolved; then dilute the solution with water to 20 cc. If the resulting well-mixed solution is not perfectly clear, filter it and use the clear solution for the following experiments.

**2. Action of Mineral Acids.** (a) To 2 cc. of the tantalum solution add 1 cc. of dil. HCl and shake the mixture. The precipitate is tantalic acid  $H_3TaO_4$ .

(b) In a 10 cc. graduate measure 3 cc. dil. HCl. **Quickly** add the acid to 2 cc. of tantalum solution and shake the mixture. Note that the precipitate which first forms redissolves yielding either a perfectly clear solution or one with a faint opalescence. Heat the solution to boiling and note that a precipitate does not form. Now add 1 cc. dil.  $H_2SO_4$  and observe that the solution becomes cloudy. Heat to boiling and note precipitation.

(c) To 2 cc. of tantalum solution add 1 cc. dil.  $H_2SO_4$ , shake and note the formation of a precipitate.

(d) To 2 cc. of tantalum solution add **quickly** 3 cc. of dilute  $H_2SO_4$ . Note that only a faint cloud forms. Heat the solution to boiling and observe that precipitation takes place. Compare the results obtained in (d) and (b). **Note.** The action of  $HNO_3$  on potassium tantalate is the same as that of HCl.

**3. Action of  $NH_4OH$  and  $(NH_4)_2S$ .** (a) To 2 cc. of tantalum solution add **quickly** 3 cc. dil. HCl. Now make the solution alkaline with conc.  $NH_4OH$ . The precipitate is tantalic acid. (b) Treat the suspended precipitate with  $H_2S$  and observe that the precipitate remains unchanged.

**4. Action of  $H_2O_2$  on Freshly Precipitated Tantalum Acid in the Presence of HCl.** To 4 cc. of tantalum solution contained in a small beaker, add **quickly** 6 cc. of dil. HCl and stir the solution vigorously. To the slightly turbid solution add conc.  $NH_4OH$

to alkaline reaction. Allow the precipitate of tantalic acid to settle and carefully pour off most of the clear solution. Now add dil. HCl to acid reaction and then 2 cc. in excess. Note the insolubility of the precipitate in an excess of HCl. Add 5 cc. 3 per cent  $\text{H}_2\text{O}_2$ , heat the mixture to boiling and stir it vigorously. Note that the precipitate does not completely dissolve (distinction from Cb). To show that some of the tantalic acid has gone into solution, filter off the precipitate. Make the filtrate alkaline with conc.  $\text{NH}_4\text{OH}$ , and boil it down to one-half of the bulk. Add 2 cc. of  $\text{H}_2\text{SO}_3$ , boil again to expel the excess of  $\text{SO}_2$  and then make the solution alkaline with  $\text{NH}_4\text{OH}$ . Boil the solution and note the precipitation of  $\text{H}_3\text{TaO}_4$ .

5. **Action of  $\text{Zn} + \text{HCl}$ .** To 2 cc. of tantalum solution, **quickly** add 3 cc. dil. HCl. Add 0.5 g. granulated zinc and allow the action to continue for several minutes. Note the absence of a blue coloration (distinction from Cb).

6. **Action of KF on the Fluorides of Cb and Ta.** Into a platinum crucible (note its number) introduce 25 mg.  $\text{Ta}_2\text{O}_5$ . Into another platinum crucible put 30 mg.  $\text{Cb}_2\text{O}_5$ . To each add 1 cc. of conc.  $\text{HNO}_3$  and about 2 cc. of 48 per cent HF. Place the crucibles on a sand bath or on an asbestos board and evaporate the solutions **under a hood** to dryness. Cool. Add about 1 cc. of 48 per cent HF to each and agitate each till complete solution takes place. Now add to each 0.5 g.  $\text{K}_2\text{CO}_3$  (using small portions at a time to minimize loss by spattering). The **crystalline** precipitate which forms in the crucible containing the tantalum is  $\text{K}_2\text{TaF}_7$ . Note that no precipitate forms in the crucible containing the columbium (method of separating Cb from Ta).

## URANIUM

### Reactions of Uranyl Salts

Use a solution of  $\text{UO}_2(\text{NO}_3)_2$  of strength 10 mg. U per cubic centimeter.

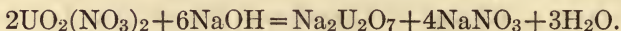
1. **Action of  $\text{H}_2\text{S}$ .** Introduce into a small beaker 2 cc. of uranium nitrate solution. Add 2.5 cc. dil. HCl and dilute the solution to 25 cc. Pass in  $\text{H}_2\text{S}$ . Note the absence of a precip-



itate. Heat the solution to boiling and treat again with  $\text{H}_2\text{S}$ . Observe that no precipitation takes place.

2. **Action of  $\text{NH}_4\text{OH}$ .** To 2 cc. of uranium nitrate solution add 1 drop of dil.  $\text{NH}_4\text{OH}$ . The yellow amorphous precipitate is ammonium uranate  $(\text{NH}_4)_2\text{U}_2\text{O}_7$ . Add 2 cc. dil.  $\text{NH}_4\text{OH}$  in excess and observe that the precipitate is insoluble in excess. Dilute the mixture with an equal volume of water, mix thoroughly and divide the suspended precipitate into two equal portions. To one, add 10 drops of a saturated aqueous solution of  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ . To the other add 1 cc. of a saturated solution of  $(\text{NH}_4)_2\text{CO}_3$ . Observe that in each case the precipitate dissolves.

3. **Action of  $\text{NaOH}$ .** Treat 2 cc. of uranium nitrate solution with one drop of  $\text{NaOH}$  solution and then add 1 cc. in excess. The yellow precipitate is  $\text{Na}_2\text{U}_2\text{O}_7$ . Note that it is insoluble in excess of the reagent.



Now add 3 cc. of 3 per cent  $\text{H}_2\text{O}_2$  and mix thoroughly. Note that the precipitate dissolves forming a deep yellow solution.

4. **Action of  $(\text{NH}_4)_2\text{S}$ .** To 2 cc. of uranium nitrate solution in a test-tube add 2 cc. of dil.  $\text{NH}_4\text{OH}$ . What is the yellow precipitate which forms (see Exp. 2)? Now pass in  $\text{H}_2\text{S}$  for one-half minute and observe the change in the color of the precipitate from yellow to chocolate brown, due to the formation of  $\text{UO}_2\text{S}$ . Divide the mixture into two equal portions. To one add an equal volume of dil.  $\text{HCl}$ . To the other add an equal volume of  $(\text{NH}_4)_2\text{CO}_3$  and warm the mixture. Note that the precipitate dissolves in each case.

5. **Action of  $(\text{NH}_4)_2\text{CO}_3$ .** (a) In a test-tube treat 2 cc. of uranium nitrate solution with 1 drop of  $(\text{NH}_4)_2\text{CO}_3$  solution and shake the tube for about a minute. The precipitate is a double salt of  $(\text{NH}_4)_2\text{CO}_3$  and  $(\text{UO}_2)\text{CO}_3$ . Now add  $(\text{NH}_4)_2\text{CO}_3$  drop by drop with shaking until the precipitate dissolves. Boil down the solution in an evaporating dish to about one-half the original volume and note the precipitation of  $(\text{NH}_4)_2\text{U}_2\text{O}_7$ .

(b) **The Precipitation of  $\text{Na}_2\text{U}_2\text{O}_7$  from an  $(\text{NH}_4)_2\text{CO}_3$  Solution of Uranium.** To 2 cc. of uranium nitrate solution add 1 drop of  $(\text{NH}_4)_2\text{CO}_3$  and shake till precipitation takes place. Now add  $(\text{NH}_4)_2\text{CO}_3$  (1 drop at a time with shaking) till a clear solution

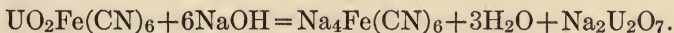


results. To the clear solution add a little NaOH. The precipitate is  $\text{Na}_2\text{U}_2\text{O}_7$ .

**6. Action of  $\text{Na}_2\text{CO}_3$ .** In a test-tube treat 2 cc. of uranium nitrate solution with 1 drop of  $\text{Na}_2\text{CO}_3$  solution and shake the solution for a minute. Observe that no precipitate forms. **Note.** In more concentrated solutions, e.g., one containing 100 mg. U per cc., a precipitate of sodium uranyl carbonate forms  $2\text{Na}_2\text{CO}_3 \cdot \text{UO}_2\text{CO}_3$ . This precipitate is moderately soluble in water, hence it does not form in dilute solutions. It is soluble in an excess of  $\text{Na}_2\text{CO}_3$  but more readily in  $\text{NaHCO}_3$  solution. To the above solution in the tube add NaOH and note the precipitation of  $\text{Na}_2\text{U}_2\text{O}_7$ .

**7. Action of  $\text{H}_2\text{O}_2$ .** To 2 cc. of uranium nitrate solution add 3 drops of 3 per cent  $\text{H}_2\text{O}_2$ . The white gelatinous precipitate is hydrated uranium tetroxide  $\text{UO}_4$ . Now add 3 or 4 drops of  $\text{Na}_2\text{CO}_3$  solution and note that the precipitate dissolves with the formation of a reddish-yellow solution. The colored compound is said to be uranyl sodium peruranate having the formula  $(\text{UO}_2)\text{Na}_2\text{U}_2\text{O}_8$  (J. Aloy).

**8. Action of  $\text{K}_4\text{Fe}(\text{CN})_6$ .** Treat 2 cc. of uranium nitrate solution with a few drops of  $\text{K}_4\text{Fe}(\text{CN})_6$ . The reddish-brown precipitate is  $(\text{UO}_2)_2\text{Fe}(\text{CN})_6$ . Divide the suspended precipitate into three equal portions. To the first portion, add a few drops of NaOH. Note that the precipitate becomes yellow due to the formation of  $\text{Na}_2\text{U}_2\text{O}_7$  (distinction from the corresponding copper compound).



Treat the second portion with 2 cc. dil. HCl and heat the mixture to boiling. Observe that the precipitate dissolves with the formation of a yellow solution. To the third portion, add 2 cc.  $(\text{NH}_4)_2\text{CO}_3$  solution and warm the mixture. Note that a clear yellow solution results.

**9. Action of  $\text{Na}_2\text{HPO}_4$ .** To 2 cc. of uranium nitrate solution add a little  $\text{Na}_2\text{HPO}_4$  solution. The yellowish-white precipitate is  $\text{UO}_2\text{HPO}_4 \cdot x\text{H}_2\text{O}$ . On separate small portions of the precipitate try the action of dil. HCl and of  $\text{HC}_2\text{H}_3\text{O}_2$ . **Note.** In the presence of  $\text{NH}_4$  salts, yellowish-white ammonium uranyl phosphate  $\text{NH}_4(\text{UO}_2)\text{PO}_4 \cdot x\text{H}_2\text{O}$  is thrown down. This precipitate

like the one above is insoluble in acetic but soluble in mineral acids.

**10. Action of  $\text{Zn} + \text{HCl}$ .** In a test-tube treat 2 cc. of uranium nitrate solution with 1 cc. of conc.  $\text{HCl}$  and a piece of zinc. Warm the mixture and allow the action to continue for about a minute. Observe the change in color from bright yellow to green. The color is best seen by pouring the solution (after the action has proceeded for about a minute) into another test-tube and examining the latter against a white background.

### The Elements of the Ceria Earths

This group includes the elements, Ce, La, Pr, Nd and Sa.

#### CERIUM

Use a solution of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  of strength 10 mg. Ce per cubic centimeter.

**1. Action of  $\text{NH}_4\text{OH}$ .** (a) To 2 cc. of cerium nitrate solution add 1 drop of dil.  $\text{NH}_4\text{OH}$  and then 1 cc. in excess. Note that the white precipitate of  $\text{Ce}(\text{OH})_3$  is insoluble in excess of the reagent and that it takes on a violet tinge on exposure to air. Add an excess (3 cc.) of dil.  $\text{HCl}$ , agitate the mixture and observe that the precipitate dissolves. (b) In a test-tube treat 2 cc. of cerium nitrate solution with 2 or 3 drops of a strong aqueous solution of  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ . Add a small piece of litmus paper and then dilute  $\text{NH}_4\text{OH}$  to alkaline reaction. Note the non-formation of a precipitate (distinction from Y).

**2. Action of  $\text{NaOH}$ .** Treat 2 cc. of cerium nitrate solution with 2 drops of  $\text{NaOH}$  solution and add 1 cc. in excess. Note that the hydroxide is insoluble in excess.

**3. Action of  $(\text{NH}_4)_2\text{S}$ .** To 2 cc. of cerium nitrate solution add 1 cc. of dil.  $\text{NH}_4\text{OH}$  and treat the mixture with  $\text{H}_2\text{S}$ . Note that the precipitate remains unchanged and that it is insoluble in excess.

**4. Action of  $\text{Na}_2\text{CO}_3$ .** In a test-tube treat 2 cc. of cerium nitrate solution with one drop of  $\text{Na}_2\text{CO}_3$  solution and then add 1 cc. in excess. The white gelatinous precipitate is cerous car-

bonate. Shake the suspended precipitate vigorously and allow it to stand for about two minutes. Observe that the precipitate has become crystalline. **Note.** The same result is obtained with  $(\text{NH}_4)_2\text{CO}_3$ . The precipitate is however, soluble in a large excess of the reagent. On boiling the solution, the carbonate reprecipitates.

**5. Action of Oxalic Acid.** To 2 cc. of cerium nitrate solution, add 1 cc. of oxalic acid solution. The gelatinous precipitate is cerous oxalate. Shake the precipitate vigorously and allow it to stand for several minutes. Observe that the precipitate has become crystalline. Divide the precipitate into two equal portions. To the first, add 2 cc. of oxalic acid and observe that the precipitate does not dissolve (distinction from Zr). To the other portion add 5 cc. dil. HCl and shake the mixture vigorously. Observe that the precipitate is practically insoluble.

**6. Action of  $\text{K}_2\text{SO}_4$ .** In a test-tube treat 2 cc. of cerium solution with 2 cc. of a saturated aqueous solution of  $\text{K}_2\text{SO}_4$ . Heat the solution to boiling and observe the formation of a white crystalline precipitate. Its formula is  $\text{Ce}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4$  (distinction from Al, Be, and Y). Add to the precipitate 2 cc. dil. HCl and agitate the mixture. Observe that the precipitate dissolves.

**7. Action of HF.** In a lead or platinum crucible, treat 2 cc. of cerium nitrate solution with 2 cc. of 48 per cent HF. The gelatinous precipitate is  $\text{CeF}_3$ .

**8. Action of  $\text{Na}_2\text{S}_2\text{O}_3$ .** To 2 cc. of cerium nitrate solution add 0.2 g.  $\text{Na}_2\text{S}_2\text{O}_3$ . Shake the tube till solution takes place and then heat the solution to boiling. The slight turbidity which forms is due to the separation of sulphur, but no appreciable amount of cerium is carried down (distinction from Zr and Th).

**9. Action of  $\text{H}_2\text{O}_2$ .** (a) Treat 2 cc. of cerium nitrate solution in a test-tube with 1 cc. of 3 per cent  $\text{H}_2\text{O}_2$ . Observe that no precipitate or coloration is formed. Now add 1 cc. of dil.  $\text{NH}_4\text{OH}$  and observe the formation of a reddish-orange precipitate resembling  $\text{Fe}(\text{OH})_3$ . The reddish precipitate is called cerium perhydroxide and possesses the formula  $\text{Ce}(\text{OH})_3 \cdot \text{OOH}$ . The same result is obtained if the order of the addition of the reagent is reversed; i.e., if the  $\text{H}_2\text{O}_2$  is added to the white precipitate of  $\text{Ce}(\text{OH})_3$  formed by adding 1 cc. of dil.  $\text{NH}_4\text{OH}$  to 2 cc. of cerium solution. This reaction serves as a very sensitive test for Ce.



(b) **Sensitiveness of the Test.** In a 100 cc. graduated cylinder, dilute 1 cc. of cerium nitrate solution with water to 100 cc. Mix thoroughly and reserve some of this solution for Exp. 10b below. To 2 cc. of this solution (.02 mg. Ce) add 1 drop of dilute  $\text{NH}_4\text{OH}$  and 1 drop of 3 per cent  $\text{H}_2\text{O}_2$ . Note the yellow color of the solution.

**10. Action of  $\text{H}_2\text{O}_2$  in  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  Solution.** (a) To 2 cc. of cerium nitrate solution add 1 cc. of  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  solution and 1 cc. of 3 per cent  $\text{H}_2\text{O}_2$ . Shake the solution for several minutes and allow it to stand. Observe that the yellow color becomes brown and that finally a reddish precipitate forms. This is a very sensitive test.

(b) **Sensitiveness of the Test.** To 2 cc. of the dilute cerium solution reserved in Exp. 9b add 1 drop of  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  solution and boil. Now add 1 drop of 3 per cent  $\text{H}_2\text{O}_2$  and note the yellow turbidity which results.

**11. Action of Br and NaOH.** In a test-tube treat 1 cc. of cerium solution with 1 cc. of NaOH solution and 3 cc. of a saturated aqueous solution of bromine. Shake the solution and allow it to stand. The yellow precipitate which forms is  $\text{CeO}_2 \cdot 3\text{H}_2\text{O}$  (method of separating Ce from La, Pr, and Nd).

**12. Oxidation of Cerous to Ceric Salts.**

(a) **By means of Ammonium Persulphate.** To 2 cc. of cerium nitrate solution in a test-tube add 1 cc. of dil.  $\text{H}_2\text{SO}_4$  and 0.2 g.  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ . Heat the mixture to boiling and boil for a few minutes. Note the yellow coloration (method of detecting Ce in the presence of La, Pr, Nd, and Th).

(b) **By Means of  $\text{NaBiO}_3$ .** To 2 cc. of cerium nitrate solution add 2 cc. of dil.  $\text{HNO}_3$  and 0.1 g.  $\text{NaBiO}_3$ . Warm the mixture gently and allow it to stand. Note orange color of the supernatant liquid.

(c) **By Means of  $\text{PbO}_2 + \text{HNO}_3$ .** Treat 2 cc. of cerium nitrate solution with 1 g. of  $\text{PbO}_2$  and 1 cc. of conc.  $\text{HNO}_3$ . Boil the mixture and allow it to settle. Observe the color of the clear solution.



## LANTHANUM

Use a solution of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  of strength 10 mg. La per cubic centimeter.

1. **Action of  $\text{NH}_4\text{OH}$ .** (a) To 2 cc. of lanthanum nitrate solution add 2 drops of dil.  $\text{NH}_4\text{OH}$ . The white precipitate which forms is a basic salt. Add 1 cc. of dil.  $\text{NH}_4\text{OH}$  in excess and observe that the precipitate is insoluble in excess. (b) Treat in a test-tube 2 cc. of lanthanum solution with 1 cc. of a strong aqueous solution of  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ . Now add dil.  $\text{NH}_4\text{OH}$  (about 3 cc.) until the resulting solution is alkaline. Observe that no precipitate forms (distinction from Y).

2. **Action of  $\text{NaOH}$ .** In a test-tube treat 2 cc. of lanthanum nitrate solution with 1 drop of  $\text{NaOH}$  solution. The white precipitate is  $\text{La}(\text{OH})_3$ . Add 1 cc. of  $\text{NaOH}$  in excess and observe that the precipitate is insoluble in excess. **Note.**  $\text{La}(\text{OH})_3$  is the strongest base of the rare earths. It turns red litmus blue, liberates  $\text{NH}_3$  from  $\text{NH}_4$  salts and absorbs  $\text{CO}_2$  from the air. Observe that the precipitate does not change in color on exposure to the air (distinction from Ce).

3. **Action of  $(\text{NH}_4)_2\text{S}$ .** To 2 cc. of  $\text{La}(\text{NO}_3)_3$  solution add 1 cc. of dil.  $\text{NH}_4\text{OH}$  and treat the mixture with  $\text{H}_2\text{S}$ . The white precipitate is  $\text{La}(\text{OH})_3$ .

4. **Action of  $(\text{NH}_4)_2\text{CO}_3$ .** In a test-tube treat 2 cc. of lanthanum nitrate solution with 1 drop of  $(\text{NH}_4)_2\text{CO}_3$  solution and then add 1 cc. in excess. Note that the precipitate is gelatinous when first formed, that it is practically insoluble in excess of the precipitant and that after standing the precipitate becomes crystalline. The formula for the crystalline salt is  $\text{La}_2\text{CO}_3 \cdot (\text{NH}_4)_2\text{CO}_3 \cdot 4\text{H}_2\text{O}$ . **Note.**  $\text{Na}_2\text{CO}_3$  gives a precipitate of analogous composition.

5. **Action of Oxalic Acid.** Treat 2 cc. of lanthanum nitrate solution with 1 drop of oxalic acid solution and then add 1 cc. in excess. Note that the white precipitate of lanthanum oxalate which forms is insoluble in an excess of the reagent. Allow the precipitate to settle and pour off the clear solution. To the precipitate in the tube add 5 cc. dil.  $\text{HCl}$ , mix thoroughly and heat. Observe that the precipitate dissolves (difference from Th). **Note.**  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  gives similar results.

6. **Action of  $K_2SO_4$ .** To 2 cc. of  $La(NO_3)_3$  solution add 2 cc. of a saturated aqueous solution of  $K_2SO_4$ . Shake the tube vigorously and allow it to stand for five minutes. Observe the formation of a crystalline precipitate. The formula for the precipitate is  $La_2(SO_4)_3 \cdot 3K_2SO_4$ . **Note.**  $La_2(SO_4)_3$  is more soluble in cold than in hot water. 100 parts of water at  $0^\circ$  dissolve 3 g. of the salt while at  $100^\circ$  only 0.3 g. are dissolved.

7. **Action of HF.** In a lead or platinum crucible, treat 2 cc. of lanthanum nitrate solution with 1 cc. of 48 per cent HF. The white gelatinous precipitate is  $LaF_3 \cdot 3H_2O$ .

8. **Action of  $Na_2S_2O_3$ .** To 2 cc. of lanthanum nitrate solution add 0.2 g.  $Na_2S_2O_3$ . Shake the tube till the salt dissolves. Heat the solution to boiling. The cloud which forms is due to the separation of sulphur resulting from the decomposition of some of the thiosulphate; but no La precipitates.

### Praseodymium and Neodymium

In 1885 Auer von Welsbach showed that the element didymium was composed of the two elements praseodymium and neodymium. The salts of the former are green while those of the latter are pink or violet. They may be identified by the characteristic absorption spectra which are given by the solutions of their soluble salts. Pr gives bands in the blue and violet, while Nd shows bands in the yellow and green. In their chemical properties, the salts of these metals resemble each other so closely, that up to the present time it has not been possible by ordinary analytical reactions to separate them. Von Welsbach effected their separation by a long series of fractional crystallizations of their double alkali nitrates.

#### PRASEODYMIUM

Use a solution of  $Pr(NO_3)_3 \cdot 6H_2O$  of strength 10 mg. Pr per cubic centimeter.

1. **Action of  $NH_4OH$  and  $(NH_4)_2S$ .** (a) To 2 cc. of Pr solution add 1 drop of dil.  $NH_4OH$  and then 1 cc. in excess. The slimy green precipitate is  $Pr(OH)_3$ . **Note.**  $NaOH$  gives the same product.

(b) Pass  $\text{H}_2\text{S}$  into the suspended precipitate and observe that there is no visible change. **Note.** The sulphide does not form in the wet way.

**2. Action of  $\text{Na}_2\text{CO}_3$ .** Treat in a test-tube 2 cc. of  $\text{Pr}(\text{NO}_3)_3$  solution with 2 drops of  $\text{Na}_2\text{CO}_3$  solution. Note the formation of a green precipitate. Now add 1 cc. of  $\text{Na}_2\text{CO}_3$  in excess, shake and allow the tube to stand. Observe that the precipitate becomes crystalline. Its formula is  $\text{K}_2\text{CO}_3 \cdot \text{Pr}_2(\text{CO}_3)_3 \cdot 12\text{H}_2\text{O}$ .

**3. Action of Oxalic Acid.** To 2 cc. of  $\text{Pr}(\text{NO}_3)_3$  solution, add 1 drop of oxalic acid solution and then add 1 cc. in excess. The light green precipitate which forms is  $\text{Pr}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ . Pour off the clear solution, add 5 cc. of dil.  $\text{HCl}$  and heat the mixture to boiling. Observe that the precipitate does not readily dissolve.

**4. Action of  $\text{K}_2\text{SO}_4$ .** In a test-tube treat 2 cc. of  $\text{Pr}(\text{NO}_3)_3$  solution with 2 cc. of a saturated aqueous solution of  $\text{K}_2\text{SO}_4$ . Shake the tube vigorously for one minute and allow it to stand for fifteen minutes. The crystalline precipitate which separates is  $3\text{K}_2\text{SO}_4 \cdot \text{Pr}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ .

**5. Action of  $\text{HF}$ .** In a lead or platinum crucible, treat 2 cc. of  $\text{Pr}(\text{NO}_3)_3$  with 2 cc. of 48 per cent  $\text{HF}$ . The gelatinous precipitate is  $\text{PrF}_3$ .

**6. Action of  $\text{Na}_2\text{S}_2\text{O}_3$ .** To 2 cc. of  $\text{Pr}(\text{NO}_3)_3$  in a test-tube, add 0.2 g.  $\text{Na}_2\text{S}_2\text{O}_3$ . Shake the tube till solution takes place. Now heat the solution to boiling. The slight cloud which forms is due to the separation of sulphur resulting from the decomposition of some of the thiosulphate; but no Pr precipitates.

## NEODYMIUM

Use a solution of  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  of strength 10 mg. Nd per cubic centimeter.

**1. Action of  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{S}$ .** (a) To 2 cc. of  $\text{Nd}(\text{NO}_3)_3$  solution add 1 drop of dil.  $\text{NH}_4\text{OH}$  and then 1 cc. in excess. Observe that the bluish-white precipitate of  $\text{Nd}(\text{OH})_3$  is insoluble in an excess of the reagent.

(b) Pass  $\text{H}_2\text{S}$  through the suspended precipitate and note that the precipitate remains unchanged in appearance. **Note.**  $\text{Nd}_2\text{S}_3$  does not form in the wet way.

**2. Action of  $\text{Na}_2\text{CO}_3$ .** In a test-tube treat 2 cc. of  $\text{Nd}(\text{NO}_3)_3$  solution with 2 drops of  $\text{Na}_2\text{CO}_3$  solution. Note the formation of a



purplish-white gelatinous precipitate. Now add 1 cc. of  $\text{Na}_2\text{CO}_3$  in excess; shake the mixture and observe that the precipitate does not become crystalline.

3. **Action of Oxalic Acid.** To 2 cc. of  $\text{Nd}(\text{NO}_3)_3$  solution in a test-tube add 1 drop of oxalic acid and then 1 cc. in excess. The rose-colored precipitate is neodymium oxalate possessing the formula  $\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ . Allow the precipitate to settle and pour off the clear solution. To the precipitate in the tube add 5 cc. dil.  $\text{HCl}$  and heat the mixture to boiling. Observe that the precipitate does not readily dissolve.

4. **Action of  $\text{K}_2\text{SO}_4$ .** In a test-tube treat 2 cc. of  $\text{Nd}(\text{NO}_3)_3$  solution with 2 cc. of a saturated aqueous solution of  $\text{K}_2\text{SO}_4$ . Shake the tube vigorously for about one-half minute and allow it to stand for about fifteen minutes. Note the crystalline precipitate which forms.

5. **Action of  $\text{HF}$ .** In a lead or platinum crucible, treat 2 cc. of  $\text{Nd}(\text{NO}_3)_3$  solution with 2 cc. of 48 per cent  $\text{HF}$ . The gelatinous precipitate is  $\text{NdF}_3$ .

6. **Action of  $\text{Na}_2\text{S}_2\text{O}_3$ .** To 2 cc. of  $\text{Nd}(\text{NO}_3)_3$  solution in a test-tube, add 0.2 g.  $\text{Na}_2\text{S}_2\text{O}_3$ . Shake the mixture till solution takes place, and then heat the solution to boiling. The cloudy solution which results is due to the separation of sulphur resulting from the decomposition of some of the thiosulphate; but no Nd precipitates.

### The Elements of the Yttria Earths

The elements belonging in this group, arranged in the order of increasing atomic weight, are Sc, Y, Eu, Tb, Gd, Dy, Ho, Er, Tu, Yb, and Lu. The most important of this group of elements are Y and Er.

#### YTTRIUM

Use a solution of  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  of strength 10 mg. Y per cubic centimeter.

1. **Action of  $\text{NH}_4\text{OH}$ ,  $(\text{NH}_4)_2\text{S}$  and  $\text{NaOH}$ .** (a) To 2 cc. of  $\text{Y}(\text{NO}_3)_3$  solution add 1 drop of dil.  $\text{NH}_4\text{OH}$  and then 1 cc. in excess. The white gelatinous precipitate is  $\text{Y}(\text{OH})_3$ . (b) Pass  $\text{H}_2\text{S}$  into the mixture and observe that the precipitate remains



unchanged. (c) To 2 cc. of  $Y(NO_3)_3$  solution add 1 drop of NaOH solution and then 1 cc. in excess. Note that the precipitate of  $Y(OH)_3$  is insoluble in excess.

**2. Action of  $Na_2CO_3$ .** In a test-tube, treat 2 cc. of  $Y(NO_3)_3$  solution with 1 drop of  $Na_2CO_3$  solution. The precipitate is  $Y_2(CO_3)_3 \cdot 3H_2O$ . Add 3 cc. of  $Na_2CO_3$  solution in excess and shake the mixture. Observe that the precipitate dissolves in an excess of the reagent. The solution contains a double carbonate of the formula  $Na_2CO_3 \cdot Y_2(CO_3)_3 \cdot 4H_2O$ .

**3. Action of  $(NH_4)_2CO_3$ .** To 2 cc. of  $Y(NO_3)_3$  solution add 1 drop of  $(NH_4)_2CO_3$  solution. Note the precipitation of  $Y_2(CO_3)_3$ . Now add an excess (3 cc.) of  $(NH_4)_2CO_3$  and agitate the mixture. Observe that the precipitate dissolves owing to the formation of a double carbonate of  $NH_4$  and Y.

**4. Action of Oxalic Acid.** In a test-tube treat 2 cc. of  $Y(NO_3)_3$  solution with 1 drop of oxalic acid solution. The white precipitate which forms is  $Y_2(C_2O_4)_3 \cdot 9H_2O$ . To the precipitate in the tube add 1 cc. of oxalic acid solution in excess and note that the precipitate is insoluble in excess. Pour off the clear solution, add 5 cc. of dil. HCl to the precipitate and shake the mixture. Observe that the precipitate is practically insoluble in dil. HCl. **Note.** Yttrium oxalate is difficultly soluble in dil. HCl. It is somewhat soluble in a boiling solution of  $(NH_4)_2C_2O_4$ , from which on cooling and diluting the oxalate is completely reprecipitated (distinction from Th).

**5. Action of  $K_2SO_4$ .** To 2 cc. of  $Y(NO_3)_3$  solution contained in a test-tube, add 2 cc. of a saturated aqueous solution of  $K_2SO_4$ . Shake the tube for a minute and then allow it to stand for ten minutes. Observe that no precipitate forms (distinction from Th, Zr and the ceria earths).

**6. Action of  $Na_2S_2O_3$ .** Treat 2 cc. of  $Y(NO_3)_3$  in a test-tube with a few crystals of  $Na_2S_2O_3$ . Shake the tube till solution takes place. Note that no precipitate forms (distinction from Th and Ti). On heating a separation of S takes place (distinction from Zr.)

**7. Action of HF.** In a lead or platinum crucible treat 2 cc. of  $Y(NO_3)_3$  solution with 1 cc. of 48 per cent HF. The gelatinous precipitate is  $YF_3$  (distinction from Al, Be, Zr, and Ti).

## ERBIUM

Use a solution of  $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  of strength 10 mg. Er per cubic centimeter.

1. **Action of  $\text{NH}_4\text{OH}$ ,  $(\text{NH}_4)_2\text{S}$  and  $\text{NaOH}$ .** (a) To 2 cc. of  $\text{Er}(\text{NO}_3)_3$  solution add 1 drop of dil.  $\text{NH}_4\text{OH}$  and then 1 cc. in excess. The gelatinous precipitate which forms is a basic salt. (b) Pass  $\text{H}_2\text{S}$  into the suspended precipitate and observe that there is no change in the appearance of the precipitate. (c) To 2 cc. of  $\text{Er}(\text{NO}_3)_3$  solution add 1 drop of  $\text{NaOH}$  and then 1 cc. in excess. Note that the precipitate is insoluble in excess.

2. **Action of  $\text{Na}_2\text{CO}_3$  and  $(\text{NH}_4)_2\text{CO}_3$ .** Treat 2 cc. of  $\text{Er}(\text{NO}_3)_3$  solution in a test-tube with 1 drop of  $\text{Na}_2\text{CO}_3$  solution and then add 3 cc. in excess. Note the solubility of the precipitate in an excess of the precipitant. (b) To 2 cc. of  $\text{Er}(\text{NO}_3)_3$  solution in a test-tube add 1 drop of  $(\text{NH}_4)_2\text{CO}_3$  solution and then add 4 cc. in excess. Note that the precipitate dissolves in excess.

3. **Action of Oxalic Acid.** In a test-tube treat 2 cc. of  $\text{Er}(\text{NO}_3)_3$  solution with 1 drop of oxalic acid solution and then add 1 cc. in excess. Note that the precipitate possesses a light rose color. Pour off the clear solution. To the precipitate in the tube add 5 cc. of dil.  $\text{HCl}$  and shake the mixture. Note that the precipitate is not readily soluble in dil.  $\text{HCl}$ .

4. **Action of  $\text{K}_2\text{SO}_4$ .** Treat in a test-tube 2 cc. of  $\text{Er}(\text{NO}_3)_3$  solution with 2 cc. of a saturated aqueous solution of  $\text{K}_2\text{SO}_4$ . Shake the solution vigorously for a minute and allow it to stand for five minutes. The precipitate is a double sulphate of K and Er. **Note.** Heating promotes precipitation. A solution of Y of the same concentration remains clear when treated with  $\text{K}_2\text{SO}_4$  and the solution heated.

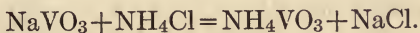
5. **Action of  $\text{Na}_2\text{S}_2\text{O}_3$ .** To 2 cc. of  $\text{Er}(\text{NO}_3)_3$  solution add 0.2 g.  $\text{Na}_2\text{S}_2\text{O}_3$  and shake the tube until solution takes place. Heat the solution to boiling. **Note.** The cloud which forms is due to the separation of sulphur which results from the decomposition of some of the thiosulphate; but no Er precipitates.

## GROUP 3B

## VANADIUM

Use a solution of  $\text{NaVO}_3$  of strength 5 mg. V per cubic centimeter.

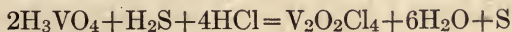
1. **Action of  $\text{NH}_4\text{Cl}$ .** In a test-tube treat 2 cc. of  $\text{NaVO}_3$  solution with 0.5 g.  $\text{NH}_4\text{Cl}$ . Shake the mixture vigorously and allow it to stand for several minutes. The white crystalline precipitate which forms is ammonium metavanadate  $\text{NH}_4\text{VO}_3$ .



Pour off carefully about 1 cc. of the clear solution. To the precipitate remaining in the test-tube, add 1 cc. of conc.  $\text{HNO}_3$ . Observe that the precipitate dissolves completely yielding a yellow solution. Transfer the solution to a small evaporating dish, evaporate (under hood) to dryness and ignite the residue. The latter is  $\text{V}_2\text{O}_5$ . Observe that it is fusible but not volatile. **Note.** When perfectly pure  $\text{V}_2\text{O}_5$  is orange-red in color.

2. **Action of  $\text{NH}_4\text{OH}$ .** (a) To 1 cc. of  $\text{NaVO}_3$  solution add 1 cc. of dil.  $\text{NH}_4\text{OH}$ . Observe that no change takes place. (b) Dilute with water 1 cc. of  $\text{NaVO}_3$  solution to 10 cc., mix thoroughly and divide the solution into 2 equal portions. To one portion add 1 drop of dil.  $\text{HCl}$  and to the other 1 drop of dil.  $\text{HNO}_3$ . Observe that in each case the solution becomes yellow. Now add a few drops of dil.  $\text{NH}_4\text{OH}$  to each, making each alkaline. Note that the color deepens in each case.

3. **Action of  $\text{H}_2\text{S}$ .** In a small beaker treat 5 cc. of  $\text{NaVO}_3$  solution with 2.5 cc. dil.  $\text{HCl}$ . Dilute the solution with water to 25 cc. and treat it with  $\text{H}_2\text{S}$  for about a minute. Note the separation of sulphur. Filter and catch the filtrate in a test-tube. Observe that the filtrate is blue, due to the reduction of the vanadate to a divanadyl salt.



4. **Action of  $(\text{NH}_4)_2\text{S}$ .** (a) In a test-tube treat 2 cc. of  $\text{NaVO}_3$  solution with 2 cc. of dil.  $\text{NH}_4\text{OH}$  and then bubble  $\text{H}_2\text{S}$  through the



solution. Note the changes in color from reddish-yellow to violet-red. **Note.** It is probable that a thio salt,  $((\text{NH}_4)_3\text{VS}_4)$  forms.

(b) **Formation and Properties of  $\text{V}_2\text{S}_5$ .** Acidify the above solution by slowly adding to it 5 cc. of dil.  $\text{HCl}$ . When effervescence ceases, filter off the  $\text{V}_2\text{S}_5$  and wash it twice with 5 cc. portions of water. Puncture the filter and wash the precipitate into a test-tube with about 5 cc. of water. Allow the precipitate to settle and carefully decant the water. Divide the suspension of  $\text{V}_2\text{S}_5$  into three equal portions. To the first in a test-tube add 2 cc. of dil.  $\text{HNO}_3$  and boil the mixture for a minute. Observe that the precipitate dissolves with the separation of sulphur. Treat the second portion with 2 cc. of dil.  $\text{NH}_4\text{OH}$  and heat the mixture to boiling. Note that the precipitate dissolves with the formation of a yellow solution. To the third portion in a test-tube add 2 cc. of  $\text{NaOH}$  solution. Note how readily solution takes place.

#### 5. Action of Reducing Agents.

(a) **Tartaric Acid.** To 2 cc. of  $\text{NaVO}_3$  solution add a few drops of a saturated aqueous solution of  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ . Observe the reddish-yellow color of the solution. Now boil the solution for a few moments and observe the further change in color from green to blue. **Note.** The blue color is due to the formation of a divanadyl salt  $(\text{V}_2\text{O}_2)_{++}^{++}$ .

(b)  **$\text{SnCl}_2$ .** Treat 2 cc. of  $\text{NaVO}_3$  solution in a test-tube with 1 cc. of  $\text{SnCl}_2$  solution and heat the tube to boiling. Note the blue color.

(c) **Oxalic Acid.** To 2 cc. of  $\text{NaVO}_3$  solution add 1 cc. of oxalic acid solution and heat the tube to boiling. Note the changes in color from yellow to blue.

(d)  **$\text{H}_2\text{SO}_3$ .** In a test-tube treat 2 cc. of  $\text{NaVO}_3$  solution with 1 cc. of dil.  $\text{HCl}$  and 0.2 g. anhydrous  $\text{Na}_2\text{SO}_3$ . Boil the solution and note the blue color which develops.

(e)  **$\text{Zn} + \text{HCl}$ .** To 2 cc. of  $\text{NaVO}_3$  solution in a test-tube add 1 cc. of dil.  $\text{HCl}$  and a small piece of zinc. Heat the tube to boiling and note reduction.

6. **Action of  $\text{H}_2\text{O}_2$ .** (a) Treat 2 cc. of  $\text{NaVO}_3$  solution with 1 cc. of dil.  $\text{HCl}$  and 2 drops of 3 per cent  $\text{H}_2\text{O}_2$ . Note that the solution becomes red due to the formation of pervanadic acid ( $\text{HVO}_4$ ).

(b) **Delicacy of the Test.** Dilute 1 cc. of  $\text{NaVO}_3$  solution with

water to 25 cc. To 2 cc. of the well-mixed solution add 1 drop of dil. HCl and 1 drop of 3 per cent  $\text{H}_2\text{O}_2$ . Note that the solution acquires a light yellow color.

**7. The Oxidation of a Vanadyl Salt to a Vanadate by Means of  $\text{Na}_2\text{O}_2$  in NaOH Solution.** In a test-tube treat 2 cc. of  $\text{NaVO}_3$  solution with 2 cc. of dil.  $\text{NH}_4\text{OH}$ . Pass  $\text{H}_2\text{S}$  into the solution until it becomes violet. Transfer the solution to a small beaker and add 5 cc. of dil.  $\text{HNO}_3$ . Note the separation of  $\text{V}_2\text{S}_5$ . Boil the mixture for one or two minutes and observe that the  $\text{V}_2\text{S}_5$  dissolves, forming a blue solution. (This blue solution contains a divanadyl salt). Filter off the sulphur which separates and catch the filtrate in an evaporating dish. Render the solution alkaline with NaOH, add 0.2 g.  $\text{Na}_2\text{O}_2$  and boil down to about 0.5 cc. Acidify the solution with dil.  $\text{HNO}_3$ , stirring the mixture thoroughly before testing with litmus and finally add a few drops of 3 per cent  $\text{H}_2\text{O}_2$ . A reddish-brown color shows the presence of a vanadate.

## GROUP V. LITHIUM, RUBIDIUM AND CAESIUM

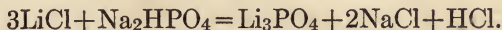
### LITHIUM

Use a solution of LiCl of strength 10 mg. Li per cubic centimeter.

**1. Action of  $\text{H}_2\text{PtCl}_6$ .** Evaporate 2 cc. of LiCl solution to 0.5 cc. Cool. Add three drops of a 10 per cent  $\text{H}_2\text{PtCl}_6$  solution and stir the mixture with a glass rod. Note that no precipitate forms (distinction from K,  $\text{NH}_4$ , Rb and Cs).

**2. Action of  $\text{Na}_3\text{Co}(\text{NO}_2)_6$ .** To 2 cc. of LiCl solution add an equal volume of  $\text{Na}_3\text{Co}(\text{NO}_2)_6$  solution. Shake the mixed solution. Note the absence of a precipitate (distinction from K,  $\text{NH}_4$ , Cs and Rb).

**3. Action of  $\text{Na}_2\text{HPO}_4$ .** In a test-tube treat 2 cc. of LiCl solution with 1 cc. of  $\text{Na}_2\text{HPO}_4$  solution. Heat the tube to boiling and note the formation of a crystalline precipitate.



**Note.** For complete precipitation, NaOH solution should be added with the  $\text{Na}_2\text{HPO}_4$  until the resulting mixture is just alkaline.

The mixture should then be evaporated to dryness and the residue treated with a little water to which some  $\text{NH}_4\text{OH}$  has been added. Under these conditions very small amounts of Li will yield a precipitate of  $2\text{Li}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ .

4. **Action of KF.** To 2 cc. of LiCl solution add 1 cc. KF solution. The precipitate is LiF (distinction and method of separation from K, Rb and Cs and from Na when the latter is not present in too large amount).

5. **Action of  $(\text{NH}_4)_2\text{CO}_3$ .** (a) In a test-tube treat 2 cc. of LiCl solution with 2 drops of dil.  $\text{NH}_4\text{OH}$  and 1 cc. of  $(\text{NH}_4)_2\text{CO}_3$  solution. Note that no precipitate forms. (b) Evaporate 10 cc. of LiCl solution to 2 cc. Cool the solution thoroughly and transfer it to a test-tube. Add 2 drops of dil.  $\text{NH}_4\text{OH}$  and 1 cc. of  $(\text{NH}_4)_2\text{CO}_3$  solution. Heat and shake the tube. The crystalline precipitate which forms is  $\text{Li}_2\text{CO}_3$ . Allow the precipitate to settle and decant the clear solution. Dissolve the precipitate in a little dil. HCl and reserve this solution for the flame and spectroscopic tests.

**Note.**  $\text{LiCO}_3$  is about one-half as soluble at  $100^\circ$  as it is at  $10^\circ$ ; hence heating favors precipitation.  $\text{LiCO}_3$  is prevented from precipitating by the presence of a considerable quantity of alkali or  $\text{NH}_4$  salts. Hence this reaction is not suitable for the detection of Li.

6. **Flame and Spectroscopic Tests.** Dip a platinum wire into the solution of LiCl formed at the end of Exp. 5 and hold it in the flame. Dip again and hold in the flame and repeat this operation until sufficient salt fuses on the wire to give a crimson color to the flame which lasts for a number of seconds. Examine the flame with a spectroscope and record your observations. **Note.** In the presence of much Na, the color is obscured, but may be seen through a cobalt glass. Anhydrous LiCl is soluble in a mixture of ether and alcohol (method of separation from the remaining metals of this group).

## RUBIDIUM

Use a solution of RbCl of strength 10 mg. Rb per cubic centimeter.

1. **Action of  $\text{H}_2\text{PtCl}_6$ .** Evaporate 2 cc. of RbCl solution to 0.5 cc. Cool. Add 3 drops of 10 per cent  $\text{H}_2\text{PtCl}_6$ . The precipitate is  $\text{Rb}_2\text{PtCl}_6$ .



2. **Action of  $\text{Na}_3\text{Co}(\text{NO}_2)_6$ .** To 2 cc. of  $\text{RbCl}$  solution add 2 cc. of  $\text{Na}_3\text{Co}(\text{NO}_2)_6$  solution. Shake and observe the formation of a yellow precipitate.

3. **Action of  $\text{SbCl}_3$ .** In a test-tube treat 2 cc. of  $\text{RbCl}$  solution with 3 cc. of  $\text{SbCl}_3$  solution (containing 100 mg.  $\text{Sb}$  as  $\text{SbCl}_3$  in 1 cc. of  $\text{HCl}$  1 : 1). Shake the mixed solution and observe that no precipitate forms.

4. **Action of  $\text{H}_2\text{SnCl}_6$ .** Treat 1 cc. of  $\text{RbCl}$  solution in a test-tube with 1 cc. of conc.  $\text{HCl}$  and 2 cc. of  $\text{SnCl}_4$  solution (containing 100 mg.  $\text{Sn}$  as  $\text{SnCl}_4$  per cubic centimeter). Shake the mixed solution and observe that no precipitate forms (distinction from  $\text{Cs}$ ).

5. **Flame Coloration.** Evaporate 5 cc. of  $\text{RbCl}$  solution to a few drops. Dip platinum wire into the solution and hold it in the flame. Observe the violet color imparted to the flame.

6. **Spectroscopic Test.** Examine the  $\text{Rb}$  flame with a spectroscope. Note the violet bands which are more intense than the line given by  $\text{K}$ .

## CAESIUM

Use a solution of  $\text{CsNO}_3$  of strength 10 mg.  $\text{Cs}$  per cubic centimeter.

1. **Action of  $\text{H}_2\text{PtCl}_6$ .** Evaporate 2 cc. of  $\text{CsNO}_3$  solution to 0.5 cc. By means of a dropper, add 3 drops of 10 per cent  $\text{H}_2\text{PtCl}_6$  solution. The precipitate is  $\text{Cs}_2\text{PtCl}_6$ .

2. **Action of  $\text{Na}_3\text{Co}(\text{NO}_2)_6$ .** To 2 cc. of  $\text{CsNO}_3$  solution in a test-tube add 2 cc. of  $\text{Na}_3\text{Co}(\text{NO}_2)_6$  solution. Shake the tube and observe the formation of a yellow precipitate.

3. **Action of  $\text{SbCl}_3$ .** In a test-tube treat 2 cc.  $\text{CsNO}_3$  solution with 3 cc. of  $\text{SbCl}_3$  solution (containing 100 mg.  $\text{Sb}$  as  $\text{SbCl}_3$  in 1 cc. of  $\text{HCl}$  1 : 1). Shake the tube vigorously for one-half minute and note the formation of a crystalline precipitate (distinction and method of separation of  $\text{Cs}$  from all the alkali metals including  $\text{NH}_4$ ).

4. **Action of  $\text{H}_2\text{SnCl}_6$ .** To 1 cc.  $\text{CsNO}_3$  solution add 1 cc. of conc.  $\text{HCl}$  and 2 cc. of  $\text{SnCl}_4$  solution (containing 100 mg.  $\text{Sn}$  as  $\text{SnCl}_4$  per cubic centimeter). Shake the tube vigorously. The white crystalline precipitate which forms is  $\text{Cs}_2\text{SnCl}_6$ . (distinction from  $\text{K}$  and  $\text{Rb}$ ). **Note.**  $\text{NH}_4$  salts give a similar pre-

precipitate with this reagent, hence they must be removed before using this reagent to test for Cs.

**5. Flame Coloration.** Introduce into the Bunsen flame a few drops of  $\text{CsNO}_3$  solution on a platinum wire and observe the red-dish-violet color imparted to the flame.

**6. Spectroscopic Test.** With a spectroscope examine the flame given by Cs salts and note the characteristic light blue lines.





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